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FACULDADE E ODONTOLOGIA DE PIRACICABA

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CIRURGIÃ-DENTISTA

CARACTERÍSTICAS DA UNIÃO À CERÂMICA DE ZIRCÔNIA TETRAGONAL POLICRISTALINA CONTENDO ÍTRIO

TESE APRESENTADA À FACULDADE DE ODONTOLOGIA DE PIRACICABA, UNIVERSIDADE ESTADUAL DE CAMPINAS, COMO PARTE DOS REQUISITOS PARA OBTENÇÃO DO TÍTULO DE DOUTORA EM CLÍNICA ODONTOLÓGICA, ÁREA DE DENTÍSTICA.

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RESUMO

Cerâmicas de zircônia tetragonal policristalina contendo ítrio (Y-TZP) apresentam propriedades mecânicas superiores as das demais cerâmicas odontológicas. No entanto, a técnica de cimentação mais adequada a estes materiais ainda não foi determinada. Os objetivos deste estudo foram: 1) Revisar a literatura a respeito de cerâmicas Y-TZP e seu uso em odontologia; 2) Avaliar o efeito de diferentes intensidades de energia do laser de Er:YAG e do jateamento com partículas de Al_2O_3 na rugosidade superficial e nas características morfológicas de cerâmicas Y-TZP e 3) Investigar a influência de diferentes tratamentos de superfície e *primers* para metal na resistência de união de dois cimentos resinosos a cerâmica Y-TZP. A análise da rugosidade superficial e das características morfológicas foi realizada em duas cerâmicas Y-TZP: Cercon Smart Ceramics e Procera Zirconia. Trinta placas de cada cerâmica foram separadas em cinco grupos experimentais de acordo com o tratamento de superfície recebido [nenhum tratamento (Controle), jateamento com partículas de Al_2O_3 ou irradiação com laser de Er:YAG em diferentes intensidades de energia (200mJ, 400mJ ou 600mJ)]. Após o respectivo tratamento superficial, as placas foram cobertas com ouro e a rugosidade superficial média (Ra, mm) foi mensurada em microscopia confocal. Características morfológicas das superfícies foram observadas em microscopia óptica e eletrônica de varredura. Os resultados demonstraram que a irradiação com laser nas intensidades de 400mJ e 600mJ promoveu aumento acentuado da rugosidade superficial, além da formação de fendas, perda de massa e alteração de cor. A irradiação com 200mJ de intensidade e o jateamento com partículas de Al_2O_3 resultaram em alterações superficiais menos agressivas que as altas intensidades do laser. Para a análise da resistência de união, 240 placas de cerâmica (Cercon Smart Ceramics) e 240 fragmentos de dentina com extremidade recortada em formato cilíndrico (0,8mm de diâmetro) foram distribuídos em 24 grupos (n=10) de acordo com a combinação entre tratamento de superfície (nenhum, jateamento com partículas de Al_2O_3 ou irradiação com laser de Er:YAG utilizando 200mJ como intensidade de energia), *primer* para metal (nenhum, Alloy Primer, Metal Primer II ou Metaltite) e cimento resinoso (Panavia F2.0 ou Calibra). Fragmentos de dentina foram cimentados nas placas de cerâmica, os corpos-de-prova foram fixados ao aparato de microcisalhamento e o ensaio foi realizado com velocidade de 1mm/min até a fratura. O jateamento com partículas de Al_2O_3 resultou em maior resistência de união para ambos os cimentos resinosos. Comparado ao Panavia F2.0, o cimento Calibra apresentou maior resistência de união nos grupos jateados e irradiados. Os dois cimentos demonstraram comportamento semelhante nos grupos sem tratamento de superfície. Os três *primers* para metal apresentaram resultados semelhantes entre si, independentemente do tratamento da superfície e do cimento resinoso, e a resistência de união da interface cerâmica-dente aumentou com a sua utilização. Pode-se concluir que, apesar da irradiação com 200mJ de intensidade promover alterações superficiais na cerâmica Y-TZP, apenas associação do jateamento com partículas de Al_2O_3 com a aplicação de *primers* para metal constitui numa técnica efetiva para união de cimentos resinosos a estas cerâmicas.

PALAVRAS-CHAVE: cerâmicas odontológicas, zircônia, laser de Er:YAG, jateamento com Al_2O_3, rugosidade superficial, resistência de união.

ABSTRACT

Yttrium-stabilized tetragonal zirconia polycrystal (Y-TZP) ceramics present superior mechanical properties compared to other dental ceramics. However, the most adequate luting technique for these materials is unknown. The aims of this study were: 1) To review the literature regarding Y-TZP ceramics and their dental application; 2) To evaluate the effect of different energy intensities of the Er:YAG laser and of air abrasion with Al_2O_3 particles on the surface roughness and morphologic characteristics of Y-TZP ceramics, and 2) To investigate the influence of different surface treatments and metal primers on the bond strength of two resin cements to a Y-TZP ceramic. The surface roughness and morphologic features were tested in two Y-TZP ceramics: Cercon Smart Ceramics and Procera Zirconia. Thirty plates from each ceramic material were allocated into five groups according to the surface treatment received [none (control), air abrasion with Al_2O_3 particles or irradiation with Er:YAG laser with three different energy intensities (200mJ, 400mJ or 600mJ)]. After the respective surface treatment, ceramic plates were gold-coated and their mean surface roughness (Ra, mm) was measured using confocal microscopy. Morphological characteristics were examined through optical and scanning electron microscopy. Results demonstrated that irradiation with 400mJ or 600mJ increased surface roughness and created cracks, loss of mass and colour changes on ceramic surfaces. Irradiation with 200mJ and air abrasion with Al_2O_3 particles provide surface alterations less aggressive than the ones caused by higher intensities of the laser. For the bond strength evaluation, 240 plates of ceramic (Cercon Smart Ceramics) and 240 fragments of dentin trimmed into a cylindrical shape (0.8mm diameter) were assigned into 24 groups (n=10) according to the combination of surface treatment (none, air abrasion with Al_2O_3 particles, or Er:YAG laser irradiation with 200mJ of energy intensity), metal primer (None, Alloy Primer, Metal Primer II or Metaltite), and resin cement (Panavia F2.0 or Calibra). Fragments of dentin were luted to ceramic surfaces, specimens were fixed in the micro-shear device and the test was carried out at a 1mm/min speed until failure. Air *abrasion with Al_2O_3 particles resulted in increased bond strength for both resin cements. Air abraded and laser irradiated specimens presented higher bond strength with Calibra resin cement than with Panavia F2.0. Both resin cements presented similar behavior on untreated surfaces. The three metal conditioners presented similar results regardless of the surface treatment and resin cement, significantly increasing the bond strength. It could be concluded that, although irradiation with 200mJ of energy intensity promotes superficial alterations on the Y-TZP ceramic, only the association of air abrasion with Al_2O_3 particles and metal primers application constitutes an effective technique for bonding resin cements to Y-TZP ceramics.*

KEY-WORDS: *dental ceramics, zirconia, Er:YAG laser, air abrasion with Al_2O_3 particles, surface roughness, bond strength.*

SUMÁRIO

1. INTRODUÇÃO

A zircônia tetragonal policristalina estabilizada por ítrio (*yttrium stabilized tetragonal zirconia polycrystal / Y-TZP*) é um material cerâmico com propriedades mecânicas superiores as das demais cerâmicas odontológicas (Kosmac *et al.*, 1999). Cerâmicas Y-TZP exibem um mecanismo conhecido como aumento da tenacidade por transformação induzida por tensão. Quando uma fratura começa a se propagar na estrutura da cerâmica, os cristais tetragonais metaestáveis próximos a ponta da fratura se transformam na fase monoclínica estável, e esta transformação acarreta numa expansão volumétrica de 3-4% em volume, a qual induz tensões de compressão que irão opor-se à rachadura e dificultar sua propagação (Chevalier *et al.*, 1999; Piconi & Maccauro, 1999).

A boa estabilidade química e dimensional das cerâmicas Y-TZP, aliada a alta resistência à fratura e ao módulo de Young da mesma magnitude das ligas de aço inoxidável deu origem ao interesse no uso da zircônia como biomaterial cerâmico (Piconi & Maccauro, 1999). A principal aplicação deste material é a reconstrução da articulação do quadril (Piconi & Maccauro, 1999), no entanto, seu uso na prática odontológica vem sendo proposto devido à crescente demanda por restaurações livres de metal e às aprimoradas propriedades mecânicas destes materiais (Piconi & Maccauro, 1999; Wolfart et al., 2007).

O baixo potencial adesivo é uma desvantagem das cerâmicas Y-TZP. Ao contrário das cerâmicas odontológicas passíveis de condicionamento, os materiais Y-TZP são compostos de pequenas partículas sem nenhuma fase vítrea nas bordas dos cristalitos (Luthardt et al., 2002). Os procedimentos de cimentação adesiva, que incluem o condicionamento com ácido fluorídrico e a aplicação de silanos na superfície do material previamente à inserção do cimento resinoso, são ineficazes nas cerâmicas Y-TZP (Derand *et al.*, 2005; Kern & Wegner, 1998; Yoshida *et al.*, 2004). O condicionamento com ácido fluorídrico é indicado apenas para superfícies com componentes vítreos, portanto, o ácido é incapaz de criar microretenções nas superfícies internas das peças em Y-TZP (Derand *et al.*, 2005; Yoshida *et al.*, 2004). Já os silanos são recomendados para formar uma união química entre a sílica presente na superfície cerâmica e a matriz orgânica dos materiais resinosos; procedimento também descartado para sistemas de óxido de zircônio devido à ausência da sílica em sua composição (Derand *et al.*, 2005; Kern & Wegner, 1998).

Estudos recentes têm sugerido técnicas de cimentação específicas para cerâmicas Y-TZP. Estas técnicas incluem métodos de tratamento da superfície, a exemplo do jateamento com óxido de alumínio, e uso de materiais que promovam união química com ao dióxido de zircônio (Derand *et al.*, 2005; Kern & Wegner, 1998; Kosmac *et al.*, 1999; Luthy *et al.*, 2006; Wolfart *et al.*, 2007; Yoshida *et al.*, 2004).

O efeito do jateamento com partículas de Al_2O_3 na superfície interna da cerâmica Y-TZP é objeto de controvérsia na literatura (Kosmac *et al.*, 1999; Piwowarczyk *et al.*, 2005; Wolfart *et al.*, 2007; Zhang *et al.*, 2004). De acordo com Zhang et al., 2004, o jateamento pode criar microtrincas na superfície da cerâmica, enfraquecendo o material ao longo do tempo. Por outro lado, segundo Wolfart et al., 2007, a adequada união à cerâmica densa de óxido de zircônio é apenas obtida após o jateamento com óxido de alumínio. Segundo os autores, este fato indica que algum tipo alteração superficial é imprescindível para se atingir união durável à zircônia. Aparentemente, ainda são necessárias informações a respeito da real eficácia do jateamento com partículas de óxido de alumínio e de outros métodos de tratamento superficial, como a irradiação com laser de Er:YAG, na cimentação de peças de óxido de zircônio.

A utilização de vários tipos de laser tem sido proposta em Odontologia desde a década de 60. O princípio do efeito do laser sobre as superfícies é fototérmico, isto é, baseia-se na conversão de energia luminosa em calor (Coluzzi, 2004). A quantidade de energia absorvida pelas superfícies irradiadas depende de características como pigmentação e conteúdo de água, do comprimento de onda da luz laser e seu modo de emissão (Coluzzi, 2004). O laser de Er:YAG foi sugerido como forma de tratamento da superfície interna de restaurações indiretas confeccionadas em compósitos e em dissilicato de lítio (Burnett *et al.*, 2004; Gokce *et al.*, 2007). Em ambos estudos, foi observado aumento na resistência de união após a irradiação com laser. Apesar destes resultados positivos, a ação do laser de Er:YAG sobre outros materiais utilizados na confecção de restaurações indiretas, como as cerâmicas Y-TZP, precisa ser determinada.

Grupamentos do éster fosfato presentes em alguns cimentos resinosos e *primers* para metal parecem capazes de se unir a óxidos metálicos, como óxido de alumínio e óxido de zircônio (Kern & Wegner, 1998; Hummel & Kern, 2004). Kern & Wegner, 1998, sugeriram que o monômero MDP (10-metacriloxil decil diidrogenofosfato) promove união química do cimento resinoso à cerâmica densa de zircônia, capaz de resistir ao armazenamento em água. Este fato foi confirmado em estudos posteriores (Luthy et al., 2006; Wolfart et al., 2007). Inversamente, materiais à base de Bis-GMA (bisfenol A glicidil metacrilato) parecem desenvolver uma união fraca e mais sensível a degradação pela água (Kern & Wegner, 1998). Recentemente, foram introduzidos no mercado materiais específicos para aumentar a união de cimentos resinosos a ligas de metais nobres, os *primers* para metal. Em função da estrutura química das cerâmicas Y-TZP, basicamente composta de óxido de zircônio, é possível que estes *primers* interajam quimicamente com a superfície cerâmica, melhorando a união com cimentos resinosos. No entanto, estudos são necessários para avaliar o efeito dos *primers* para metal na cimentação adesiva de cerâmicas Y-TZP.

As evidências existentes a respeito da união de materiais resinosos a cerâmicas Y-TZP indicam que a técnica com melhor previsibilidade e durabilidade ainda não foi determinada. Por este motivo, os procedimentos de união a cerâmicas Y-TZP devem ser profundamente testados em estudos *in vitro,* visando identificar materiais e técnicas superiores, previamente à sua aplicação clínica.

2. PROPOSIÇÃO

O presente estudo teve os seguintes objetivos:

2.1 Revisar a literatura a respeito de cerâmicas Y-TZP, descrevendo suas principais características, aplicação clínica e a problemática relacionada à cimentação destes materiais.

2.2 Avaliar a ação de três intensidades de energia do laser de Er:YAG (200 mJ, 400 mJ e 600 mJ) e do jateamento com partículas de 53 μm de óxido de alumínio na rugosidade superficial e nas características morfológicas de cerâmicas Y-TZP;

2.3 Determinar a resistência da união dentina-cerâmica Y-TZP formada com diferentes cimentos resinosos, em função do tratamento de superfície e do uso de *primers* para metais.

3. CAPÍTULOS

Esta tese está baseada na Resolução CCPG/002/06UNICAMP que regulamenta o formato alternativo para teses de Mestrado e Doutorado. Três capítulos contendo artigos científicos compõem este estudo, conforme descrito abaixo:

Capítulo Um. Y-TZP ceramics: key concepts for clinical application.
Artigo submetido à apreciação pelo periódico **Journal of Prosthodontics**.

Capítulo Dois. Effect of Er:YAG Laser Irradiation on the Surface Roughness and Morphologic Features of Y-TZP Ceramics.
Artigo submetido à apreciação pelo periódico **Lasers in Surgery and Medicine.**

Capítulo Três. Bond strength of resin cements to a zirconia ceramic with different surface treatments.
Artigo submetido à apreciação pelo periódico **Dental Materials.**

CAPÍTULO UM

Y-TZP CERAMICS: KEY CONCEPTS FOR CLINICAL APPLICATION

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ABSTRACT

Yttrium-stabilized tetragonal zirconia (Y-TZP) ceramics have some superior mechanical properties to those of conventional ceramic systems, ensuring a broad application in Dentistry. This study aimed to present relevant information about Y-TZP ceramics gathered from peer-reviewed papers. A search of the English language peer-reviewed literature was completed using PUBMED database, from the period of 1998 to 2008. Articles that did not focus exclusively on the clinical application of Y-TZP ceramic restorations were excluded from further evaluation. Selected papers describe the chief characteristics of zirconia ceramics, and important clinical features, especially related to cementation procedures. The literature shows that, although new substances and equipment for surface preparation of zirconia ceramics are in development, the most promising luting protocol seems to be the use of air abrasion with aluminum oxide particles (silanized or not) followed by the application of resin cements or surface primers containing special reactive monomers. However, because zirconia ceramics have only recently been developed for dental applications, there is not enough clinical evidence to support any definitive cementation protocol.

INDEX WORDS: zirconia, air abrasion with aluminum oxide particles, resin cement.

INTRODUCTION

A progressive improvement in the mechanical properties of dental ceramics has lead to an increase in all-ceramic restorations.[1-3] The zirconia systems currently available for use in dentistry include ceramics with a zirconium dioxide content higher than 90%, which is the yttrium-stabilized tetragonal zirconia (Y-TZP), and glass-infiltrated ceramics with 35% partially stabilized zirconia. Because of the superior mechanical properties of Y-TZP ceramics, these materials have a wide range of clinical applications, from implant abutments and single-tooth restorations to fixed partial dentures (FPDs) involving several elements.[2-7]

In contrast to conventional dental ceramics, Y-TZP is composed of many small particles without any glassy phase at the crystallite border.[5] The absence of a silica and glassy phase impairs the effectiveness of conventional adhesive luting procedures, which include etching ceramic surfaces with hydrofluoric acid and applying silanes prior to the use of a resin cement.[1, 3, 6-11] Recent studies have suggested specific luting techniques for Y-TZP ceramics. Those include surface treatments and the use of materials with a chemical affinity for zirconium dioxide.[1-4, 6-13]

Although Y-TZP has been used as a ceramic biomaterial in medical applications since the late sixties, its use in dentistry is relatively recent.[12, 14] For this reason, it is not surprising that dentists have doubts regarding the clinical applications and cementation of this type of ceramic. This work aimed to collect information about Y-TZP ceramics in order to describe their chief structural characteristics, clinical features, manufacturing procedures, and specificities related to the luting procedure.

DENTAL CERAMICS

As a result of the good properties of dental ceramics, such as aesthetics, hardness, resistance against compression, chemical resistance, and biocompatibility, a great effort has been made to improve their weak points like brittleness, and low tensile strength. There are different ways of strengthening ceramic systems to minimize flaw propagation through the material, the most important ones being dispersion strengthening and transformation toughening.[15] Dispersion strengthening is based on the addition of a disperse phase of a different material that is capable of hindering a crack from propagating. When tiny crystals of a tough material are homogeneously distributed throughout the glass matrix, the ceramic structure is toughened and strengthened because the crack cannot propagate through the crystals as easily as it does through glass.[15] Dental ceramics can be reinforced with a wide variety of crystalline disperse phases, such as alumina, leucite, lithium disilicate and zirconia. Nevertheless, toughening depends on the crystal type, its size and volume fraction, the interparticle space and the relationship between the thermal expansion of the glass and the crystalline phase.[15]

The other method of ceramic reinforcement is based on the use of a material that undergoes microstructural changes when submitted to stress. This mechanism is known as stress-induced transformation toughening.[14-17] The crystalline structure of the zirconium dioxide experiences a transformation from a tetragonal (T) to a monoclinic (M) phase at the tips of cracks. The stress associated with expansion due to the phase transformation acts in opposition to the stress that promotes the propagation of the crack. The energy associated with crack propagation is dissipated for the T-M transformation and for overcoming the compression stresses caused by volume expansion.[14-17] Therefore, a highly intense tension will be necessary for the fracture to continue propagating.[15] The development of materials with stress-induced transformation toughening is considered one of the most remarkable innovations in the study of ceramics.[16]

Y-TZP CERAMICS

Zirconia is a name given for zirconium dioxide (ZrO_2). Zirconia is a polymorphic material, thus, it can exhibit more than one crystalline structure, depending on the temperature and pressure conditions. Polymorphic transformations are followed by changes in the density and other physical properties of the material. Pure zirconia is monoclinic (M) at room temperature. This phase is stable up to 1,170^{o}C. Under higher temperatures, it will transform into a tetragonal (T), and later into a cubic phase (C) at 2,370^{o}C. The phase transformation that occurs during cooling to room temperature is associated with a great volumetric expansion. Stresses generated by the expansion generate cracks in pure zirconia ceramics, which after being sintered between 1,500 and 1,700^{o}C, can break into pieces at room temperature. This great volumetric expansion precludes the use of pure zirconia in ceramic systems.[14, 15]

The addition of stabilizing oxides to pure zirconia allows the generation of multiphase materials. In the early stages of the development of zirconia ceramics, several dopants were tested, such as CaO, MgO, CeO_2, and Y_2O_3. Most research on zirconia ceramics for dental applications is focused on yttrium-doped ceramics.[14] The addition of 3–6 % weight of Y_2O_3 can prevent polymorphic transformation during heating and cooling. Through the ZrO_2-Y_2O_3 system, one can obtain a ceramic material consisting of the tetragonal phase only, known as yttrium tetragonal zirconia polycrystals (Y-TZP).[14, 15] There is another type of zirconia material available, glass-infiltrated zirconia ceramic. This system presents a high crystal content of aluminum and zirconium oxide and a limited vitreous phase (approximately 20wt%).[18] Commercial brands, manufacturers, classification and composition of current zirconia ceramic systems are presented in Table 1.

The stress-induced transformation toughening is a unique characteristic of Y-TZP ceramics, that gives them superior mechanical properties compared to other ceramics,[13, 19] and can explain why this material is referred by some authors as a "ceramic steel".[15, 19] The formation of compressive layers on their surface is a consequence of the toughening mechanism induced by external stresses or temperature changes.[13, 19] These layers can result in increased hardness and can have a important role in the improvement of the mechanical properties of Y-TZP materials. On the other hand, a continuing progression of phase transformation might initiate surface flaws, followed by the ejection of grains, resulting in catastrophic effects on mechanical properties, making the material more vulnerable to ageing.[14, 17]

Mechanical properties can influence the clinical behavior of all-ceramic restorations.[20] Studies have shown that Y-TZP ceramics present superior mechanical properties compared with other dental ceramics; even higher than glassy-infiltrated zirconia ceramics.[20] The flexural resistance of Y-TZP ceramics can reach values from 700 to 1200 MPa.[13, 18, 20] These values exceed the maximal occlusal loads during normal chewing.[18] Three-unit FPDs made of Y-TZP exhibited fracture resistance of more than 2,000 N, which is almost twice the value of alumina-based materials and almost three times the value of lithium disilicate-based ceramics.[21] According to Potiket et al.,2004, teeth restored with all ceramic single crowns made of Y-TZP material have fracture resistance similar to the ones with metal-ceramic restorations.[22]

CLINICAL APPLICATION AND MANUFACTURE OF Y-TZP CERAMICS

The clinical indications of indirect restorations made of zirconia ceramics include FPDs supported by teeth or implants. Because of its higher mechanical properties, this material can be used in several clinical situations, from a single-unit restoration to FPDs with multiple elements in the anterior or posterior region of the oral cavity.[21, 22] Although some manufacturers indicate that zirconia ceramics allow the fabrication of a prosthesis involving the full-arch, FPDs with a maximum of five elements demonstrated more reliable results under *in vitro* conditions.[23] This material can also be used for posts and cores or implant abutments in prosthetic dentistry.[6]

Y-TZP ceramics have some colors to simulate the tooth structure, however, they are highly opaque.[24] This radiopacity can be very useful for monitoring their marginal adaptation through radiographic analysis, especially when intrasulcular and proximal preparations are performed.[24] On the other hand, opacity might limit the aesthetic outcome of zirconia restorations compared to those made of conventional dental ceramics.

Frameworks in Y-TZP are produced using a CAD/CAM system (computer-aided design/manufacturing), which follows some stages that involve both clinical and laboratorial steps. Preparations must follow the scallop of the free gingival margin, incisal/occlusal reduction should be, at least, of 1.5mm, and axial reduction should be up to 1.0mm. Excessive tapered preparations should be avoided.[4, 24] A chamfer or rounded shoulder are recommended as finishing lines because they increase the material thickness at the restoration margins.[24] The diameter of the connector might vary according to the length of the FDP.[23, 25] It was suggested that connector diameters with 4.0 mm could be sufficient for FPDs that replace molars and for the ones involving four or more units. Higher dimensions (>4.0mm) may be necessary if excessive forces are expected, as in patients with a deep overbite, bruxism, or with history of fractured reconstructions. For shorter FPDs as well as anterior ones, smaller dimensions might be adequate.[25]

After conventional impression and die casting procedures, the tooth preparation is scanned following the CAD/CAM procedure, or the restoration is waxed up and further scanned through the CAM procedure.[26] There are two techniques for manufacturing Y-TZP frameworks.[27] In the first technique, partially sintered zirconia blocks are milled according to the shape of the restoration, but in a higher dimension to compensate for the linear shrinkage that occurs after sintering. Then, the ceramic is sintered and the framework shrinks to the final dimension.[26] In the second method, restorations of the final dimension are milled from fully sintered zirconia blocks. No further heat treatment, with associated dimensional change, is required, however, the fracture strength of fully sintered Y-TZP may be increased by hot isostatic pressing (HIP).[27] Regardless of the manufacturing technique, frameworks must be further veneered with porcelain to recreate the natural appearance of the tooth.[28]

The veneer material plays an important role on the mechanical behavior of all-ceramic bridges since it affects the stress distribution on the bridge and also contains critical flaws from which crack propagation can initiate.[29] The performance of the complex Y-TZP framework-veneer porcelain has been investigated.[29, 30] In a work testing the fast fracture behavior of veneer-framework composites for all-ceramic dental bridges, authors noted that cracks originating on the veneer layer deflected at the veneer-Y-TZP framework interface, resulting in the delamination of the veneer layer before the complete fracture of the sample at higher stress levels. The same fracture mode was observed in other studies.[30] Although this finding resulted from *in vitro* conditions, which are far different from a clinical situation, it can be clinically relevant because indicates that tougher framework materials are able to stop cracks originating on the weaker veneer layer, avoiding the catastrophic failure of the prosthesis.[29]

The load-bearing capacity of posterior four-unit FPDs produced with a pre-sintered Y-TZP material and with a fully sintered, hot isostatically pressed ceramic was investigated.[27] Results indicated that the choice of material proved to have a significant influence on the load capacity of FPDs. The fully sintered zirconia treated with HIP has been shown to possess higher bending strength compared with the pre-sintered material. This finding was justified by the discrepancies in both the density and homogeneity of the materials investigated. Specimens made of zirconium dioxide treated with HIP had a very homogenous structure, in contrast to those made of pre-sintered Y-TZP. The latter contained a greater number of pores, likely to act as stress concentrators and crack origins.[27] Nonetheless, the Y-TZP materials, either processed by HIP and fully sintered or pre-sintered, demonstrated forces at fracture that were approximately 80 to 140 % higher than the 500 N benchmark, considered as the lower limit of static load-bearing capacity for clinically acceptable bridges in the posterior region. Therefore, authors have concluded that both types of Y-TZP may be suitable for posterior four-unit all-ceramic FPDs.

Results from several investigations have shown that the mechanical properties of Y-TZP ceramics depend not only on the microstructure of the material but also on the manufacturing process of the frameworks/restorations.[14, 18, 27, 31] Studies have investigated the effect of milling, thermal alterations, and finishing and polishing procedures on the performance of zirconia ceramics. Milling can result in contradictory effects.[31] It can induce compressive layers on the surface; and those layers can improve the mechanical properties of the material. On the other hand, milling can also produce flaws that exceed the thickness of the compression layer, depending on the percentage of the T-M phase transformation, milling severity and local temperatures.[13, 31]

The consequences of different milling parameters (speed of milling and wear depth) on the characteristics of a Y-TZP ceramic have been investigated; and the results showed that they significantly affect the strength and reliability of the material.[5] The authors concluded that the methods for fabrication of zirconia structures still need to be improved, in order for restorations to fulfill their purposes with reliability. In addition, a major factor on milling is the size of the grain; the bigger the size of the abrasive, the thicker the superficial flaw.[5]

Temperature can also affect the properties of Y-TZP frameworks. It was stated that the heat generated during the application of the veneering porcelain (maximum temperature of 930^{o}C) can induce the reverse phase transformation M-T, diminishing the content of the monoclinic phase, preventing the generation of compressive layers, and, consequently affecting the properties of the material.[31] Nevertheless, another investigation has shown that tensile stresses generated by veneering with a veneering material did not cause the expected T-M transformation. Authors suggested that the tensile stresses that did not exceed 100 MPa were too low to cause a phase change.[28]

In addition, zirconia ceramics can suffer a process known as low temperature degradation (LTD).[17, 18] This aging occurs through the slow and continuous phase transformation in the presence of water or humidity.[17] A previous study found that treatments at low temperatures (250^{o}C) and under humidity did not diminish the flexural resistance of a Y-TZP material.[18] Nevertheless, chemical composition analysis through energy dispersive spectroscopy (EDS) revealed that the yttrium concentration reduced significantly after thermal aging, from 6.76 to 4.83% weight. According to the authors, reducing the yttrium percentage might affect the material's stability, making the ceramic susceptible to progressive phase transformations and decreasing the clinical serviceability of this dental ceramic material.[18]

Air abrasion with aluminum oxide particles is routinely performed to remove layers of contaminants, increasing the micro-mechanical retention between resin cement and the restoration.[2] Usually, air abrasion units use aluminum oxide particles with sizes ranging from 25 to 250µm. These particles may or may not be silica-coated (tribochemical treatment).[32] The effect of air abrasion on the mechanical properties of zirconia has been repeatedly discussed in the literature and both positive and negative results have been described.[13, 18, 32]

Some authors have stated that air abrasion increases the flexural resistance of zirconia ceramics because it induces T-M phase transformations, creating compressive layers on the surface.[13, 18, 31, 32] Apparently, the depth of the surface flaws induced by air abrasion do not exceed the thickness of the compressive layers, justifying the improved properties of air abraded surfaces.[18] Nevertheless, the flexural strength of airborne-particle abraded specimens decreases after simulated aging or after a heat treatment similar to porcelain veneer application because of the release of the compressive layer.[18, 31] Therefore, flaws induced by the airborne-particle abrasion process can be responsible for the strength degradation, if not neutralized by the region of compressive stresses.[18]

When the effects of air abrasion and milling with fine grained diamond instruments (20-40µm) were compared with the use of coarse diamond burs (125-150µm), it was observed that less severe protocols reduced surface roughness and provided the formation of compressive layers on the surface. Conversely, coarse diamond burs reduced flexural strength and the reliability of Y-TZP ceramics.[32] In a different study, air abrasion and coarse diamond burs also presented an opposite effect on the flexural resistance of a zirconia ceramic.[13] The authors added that, during milling with the diamond bur, a great amount of material was removed and sparks were commonly observed despite constant refrigeration, indicating that both stresses and temperatures were high during the operation.[13]

Tribochemical coating seems to be less effective for zirconia ceramics than for glass-infiltrated ceramics.[4, 8] In this technique, air pressure impregnates the ceramic with silica particles; and further silane application renders the impregnated surface chemically reactive to the resin cement. However, siloxane bonds (among silica, silane and resin cement) are only formed if the surface presents oxygen and silica, because both molecules present linking sites between silane and ceramic.[33] Y-TZP ceramics present higher hardness compared with systems with a glassy structure, which prevents the impregnation of silica on the surface.[33] For this reason, silane agents do not bond adequately to zirconia ceramics.[8] Although some studies have demonstrated good results with tribochemical treatment,[9, 34] one might ask the question of whether the improved bonding was caused by the siloxane bond or by the micromechanical retention; and this fact should be investigated in further studies.

According to some other studies, surface treatments such as air abrasion might increase ceramic degradation over time. Zhang et al., 2004, demonstrated that the strength of air abraded Y-TZP ceramic decreases significantly when specimens are submitted to fatigue. This might be indicative of the presence of surface flaws, which increase with cyclic load application, and negatively affect the material's properties.[35] Any further grinding or abrasion performed during the luting procedure might exacerbate superficial flaws created by air abrasion, resulting in fracture propagation.[35]

Despite the possible negative outcomes of surface treatments on the mechanical properties of Y-TZP materials, the application of resin cements to untreated surfaces apparently result in low bond strength, which is unable to resist water storage.[2] This fact might indicate that some surface alteration is fundamental in order to obtain a durable bond to zirconia.[2] Other techniques for the superficial treatment of zirconia ceramics have been described; these are plasma spray, glass pearls fused to the zirconia surface and heat-induced maturation followed by selective infiltration etching (HIM/SIE).[3, 11] It was shown that plasma spraying and fusing glass pearls to the zirconia surface improved the bond strength of resin cements to the surface. Nevertheless, these treatments were not compared to conventional methods of surface treatments for Y-TZP ceramics, such as air abrasion and tribochemical coating.[3] The plasma is a partially ionized gas containing ions, electrons, atoms and neutral species. Covalent bond formation following plasma application might be an explanation for the higher bond strengths, although this mechanism has not been fully elucidated. On the other hand, fusing glass pearls to zirconia ceramics increases the surface roughness, improving the retention of the resin cement to the surface.[3]

BONDING TO Y-TZP CERAMICS

The longevity of an indirect restoration is closely related to the integrity of the cementation line. Although the use of zirconia ceramics for dental applications is ongoing, the best method to promote a durable bond between ceramic and tooth structure is still unknown.[8] The only consensus found in the literature is that hydrofluoric acid etching and common silane agents are not effective for zirconia ceramics.[8-11]

A great diversity of materials for the fixation of all-ceramic restorations is commercially available. Those include zinc phosphate cements, conventional and resin modified glass ionomer cements, resin cements and self adhesive resin cements.[36] However, resin cements possess some advantages compared with the other classes of materials, since they have lower solubility and better aesthetic characteristics.[1, 12, 36, 37] In addition, the adhesive bond between resin cement and ceramic might increase the restoration's resistance during occlusal loads.[1, 36, 37]

The shear bond strength of eleven different types of cements to a Y-TZP ceramic was evaluated.[36] The results indicated that zinc phosphate and conventional and resin-modified glass ionomer cements were not able to form a durable bond to zirconia.[36] In another study, the authors stated that the bond strength of glass ionomer cements and of a conventional Bis-GMA-based resin-composite to zirconia ceramics is significantly lower, especially after thermal aging.[12]

There is some evidence demonstrating that a better bond to Y-TZP ceramics is obtained using resin cements with phosphate ester monomers, such as the MDP monomer.[2, 7-10, 12] The phosphate ester group might chemically bond to metal oxides like zirconium dioxide.[2, 10, 12] Wolfart et al., 2007, evaluated the durability of the bond with two resin cements (MDP-based and Bis-GMA-based) to a zirconia ceramic. The MDP-based material presented higher bond strength to zirconia surfaces air abraded with alumina particles, and this bond survived 150 days of water storage.[2] Other studies also stated that resin cements with phosphate ester groups increase the bond strength of air abraded, tribochemically coated and HIM/SIE treated surfaces.[8, 9, 11, 12]

Other monomers present in resin cements might also have chemical affinity for metal oxides.[12, 34, 36] For example, the anhidride group present in 4-META monomer and the phosphoric methacrylate ester can also chemically bond to zirconia ceramics.[12, 34] It was observed that the bond strength of a polymethylmethacrylate (PMMA) resin cement containing 4-META was initially high, however, this bond was not strong enough to resist thermal aging.[12] Water absorption by the PMMA during thermal cycling might have weakened the chemical bond.[12] On the other hand, the use of a self-adhesive cement containing phosphoric methacrylate ester resulted in bond strengths to zirconia similar to that of MDP-based resin cements after 14 days of thermal cycling and water storage.[36] In another study, this cement provided similar coping retention compared to a MDP-based resin cement and a resin-modified glass ionomer cement.[38] The mean coping removal stresses for the axial surface ranged from 6.7 MPa to 8.5 MPa, which is similar to the range of removal stress observed for gold castings when using zinc phosphate and glass ionomer cements. The authors concluded that the three cements tested are capable of retaining zirconium oxide crowns successfully, needing no additional internal surface treatment other than airborne-particle abrasion with 50-µm aluminum oxide followed by appropriate cleaning of the crown prior to cementation.[38]

A previous study[39] indicated that the application of a MDP-containing bonding/silane coupling agent is the key factor for a reliable resin bond to Y-TZP ceramics, and is not influenced by the resin luting agent used. Currently in the dental market, priming agents containing special adhesive monomers are available to improve adhesive bonding to metal alloys, the metal primers. These substances contain, besides MDP, other monomers such as VBATDT (6-(4-vinylbenzyl-n-propyl)amino-1,3,5-triazine-2,4-dithione), MEPS (thiophosphoric methacrylate) and MTU-6 (6-methacryloyloxyhexyl-2-thiouracil-5-carboxylate). Yoshida et al, 2006, stated that the bond strength between resin cement and zirconia increased significantly when surfaces were coated with a MDP-based metal primer. However, this bond could not resist thermal aging.[10] The results of this study also showed that a mixture of MDP-based metal primer with a zirconate agent (2,2-di(allyloxymethy)butyl trimethacryloyl zirconate) strengthened the bond between resin cement and zirconia ceramic. This mixture might be a clinically effective way of improving bonding to these ceramics and should be further investigated.[10]

CONCLUSIONS

Based on the scientific evidence gathered in this literature review, the following conclusions could be drawn:

- The methods for manufacturing Y-TZP frameworks and for treating surfaces previously to luting can affect the mechanical properties of zirconia ceramics. Nevertheless, the clinical implication of such modifications hasn't been determined.
- Air abrasion with aluminum oxide particles (silanized or nor) is the surface treatment most frequently indicated to improve the bond between resin cements and Y-TZP ceramics. Although some studies have indicated that some surface treatments may lower the mechanical properties of Y-TZP materials, this effect might depend on the magnitude of the protocol used.
- The use of special functional monomers able to chemically bond to zirconium dioxide, appear to improve the quality of the bond between resin cement and ceramic. Currently, these monomers are found both in resin cements and metal primer solutions.

- Although several scientific studies are currently available, clinical studies are necessary to evaluate the long-term behaviour of Y-TZP restorations and to establish which materials and techniques should be recommended for luting these restorations.

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Table 1. Commercial brands of zirconia ceramics, manufactures, classification and composition.

Commercial brand (manufacturer)	Manufacturing	Composition*
Cercon Smart Ceramics (DeguDent, Hanau, Germany)	CAM of partially sintered Y-TZP blanks	5% Y_2O_3 TZP
LAVA All-Ceramic System (3M ESPE, Seefeld, Germany)	CAM of partially sintered Y-TZP blanks	3% Y_2O_3 TZP
Procera Zirconia (Nobel Biocare, Göteborg, Sweden)	CAM of partially sintered Y-TZP blanks	4.5-5.4% Y_2O_3 TZP
IPS Zircad (IvoclarVivadent, New York, USA)	CAM of partially sintered Y-TZP blanks	4-6% Y_2O_3 TZP
DCZirkon (DCS Dental AG, Allschwil, Switzerland)	CAM of fully sintered blanks	5% Y_2O_3 TZP
Vita In-Ceram YZ Cubes (Vita Zahnfabrik, Bad Säckingen, Germany)	CAM of partially sintered Y-TZP blanks	5% Y_2O_3 TZP
Vita In-Ceram Zirconia (Vita Zahnfabrik)	Glass-infiltration processing	33% t-ZrO_2 (Ce-stabilized), 67% Al_2O_3

* According to the information provided by the manufacturers.

CAPÍTULO DOIS

EFFECT OF ER:YAG LASER IRRADIATION ON THE SURFACE ROUGHNESS AND MORPHOLOGIC FEATURES OF Y-TZP CERAMICS

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KEY WORDS: Air abrasion, Dental ceramics, Er:YAG laser, Surface roughness.

ABSTRACT

Background and objective: Surface roughness enhances the micromechanical interlocking of luting agents to ceramic surfaces. However, the most appropriate surface treatment for yttrium-stabilized tetragonal zirconia (Y-TZP) ceramics still has to be determined. This study investigated the effect of different energy intensities of the Er:YAG laser and of air abrasion with Al_2O_3 particles on the surface roughness and morphologic characteristics of high strength ceramics.

Study Design/Materials and Methods: Two Y-TZP materials were evaluated: Cercon Smart Ceramics and Procera Zirconia. Thirty plates from each ceramic material were randomly allocated into five groups according to the surface treatment received [none (control), air abrasion or irradiation with Er:YAG laser at three different energy intensities (200 mJ, 400 mJ or 600 mJ)]. After the respective surface treatment, ceramic plates were gold-coated and their surface roughness (Ra, µm) was measured using confocal microscopy. For each ceramic system, the surface roughness was analyzed through One-way ANOVA/Tukey test, with a 5% significance level. Changes in morphological characteristics of ceramics were examined through optical and scanning electron microscopy.

Results: For both zirconia-based materials, irradiation with 400mJ or 600mJ increased surface roughness and provided significant morphological changes on ceramic surfaces. Air abraded Cercon surfaces were rougher compared to the ones irradiated with 200 mJ. On the contrary, Procera surfaces irradiated with 200 mJ were rougher than the air abraded ones.

Conclusions: Laser irradiation with 400 mJ and 600 mJ seems to be an excessively strong protocol. Irradiation with 200 mJ provides mild surface alterations, with intermediary features between the effects of air abrasion with aluminum oxide particles and higher laser intensities.

INTRODUCTION

A durable and stable bond between luting cements and ceramics is fundamental for the long-term performance of all ceramic indirect restorations. Resin cements present some advantages compared to other types of luting materials such as zinc-phosphate cements and glass-ionomer cements. These include improved marginal seal, good retention, and adequate aesthetic characteristics (1,2). However, one of the key mechanisms for an adequate bond between resin cement and ceramic is the micromechanical attachment (2,3). Roughening the inner surfaces of ceramic restorations increases the area available for the penetration and in situ polymerization of resin-based materials, enhancing the mechanical bond.

Etching with 5-10% hydrofluoric acid is a well-suited surface treatment method for silica-based ceramics (2,3). Acid etching selectively removes the glassy matrix of some ceramic systems, exposing the crystalline structures, resulting in substance loss and an increase in surface roughness (2,4). However, other high strength ceramic materials, such as yttrium-stabilized tetragonal zirconia (Y-TZP) ceramics, are not suitable for acid etching since they do not present the glassy phase (4-7). For this reason, alternative methods for treating the inner surfaces of Y-TZP materials prior to luting are necessary.

Air abrasion with aluminum oxide particles is a commonly used surface treatment for ceramic materials. Air abrasion units use aluminum oxide particles with sizes ranging from 25 to 250µm. Those particles might or might not be silica-coated (tribochemical treatment) (8). The abrasive process removes loose contaminated layers, increases the area available for bonding, and improves the wettability of luting materials (6,9). Nevertheless, flaws created by air abrasion may function as crack initiators in Y-TZP materials, compromising their mechanical properties and long-term performance (10). Contrasting results observed with air abraded Y-TZP ceramics indicate that the effects of air abrasion and other methods of surface modification, such as laser irradiation, should be further investigated.

The erbium:yttrium-aluminum-garnet (Er:YAG) laser has been proposed for different clinical dentistry applications, including carious dentin removal, cavity preparation, and as a surface treatment method for indirect restorations made of lithium dissilicate and composites (10-15). In tooth substrates, Er:YAG laser produces micro-explosions during hard tissue ablation that result in macroscopic and microscopic irregularities that constitute an adhesion mechanism (10). Although there is plenty of information regarding the effects of Er:YAG irradiation on dentin and enamel structures, little is known about the use of this laser as a surface treatment for high strength dental ceramics. Therefore, the aim of the present study was to compare the surface roughness and morphologic features of untreated and air abraded surfaces of Y-TZP ceramics with those of surfaces irradiated with different energy intensities of the Er:YAG laser.

MATERIALS AND METHODS

Two Y-TZP ceramic materials were investigated in the present study: Cercon Smart Ceramics (Degudent, Hanau, Germany), which is a 5% Y_2O_3 TZP ceramic and Procera Zirconia (Nobel Biocare, Göteborg, Sweden), which is a 4.5-5.4% Y_2O_3 TZP material. Each system was industrially manufactured, and further sectioned into plates 5 x 3 x 0.75mm in size. Thirty plates from each ceramic were obtained.

The thirty plates of each ceramic were randomly divided into 5 experimental groups (n=6/ceramic system), according to the surface treatment performed. In the air abraded and lased groups, the superficial area to be further treated (1.76mm^2) was delimitated with adhesive tape.

Control: Specimens were only ultrasonically cleaned with 96% isopropanol for 3 minutes.

Air abrasion: Air abrasion was performed with 53μm aluminum oxide particles (Aquacut, Medivance Instruments Ltd. London, UK) at a 2.5 bar pressure for 15 seconds at a distance of 10mm. Then, the adhesive tape was removed and the plates were ultrasonically cleaned with 96% isopropanol for 3 minutes.

Er:YAG laser irradiation: Surfaces were coated with graphite prior to the laser irradiation to increase the absorption of energy. The laser equipment used was a Er:YAG laser (OPUS 20 Er:YAG / CO_2 Dental Laser Surgical System, Sharplan Medical Systems, Yokneam, Israel) emitting a 2.94 μm wavelength. A 1,000-μm-diameter straight-type sapphire tip was used perpendicularly to the surface in a contact mode. Surfaces were lased for 5 seconds using a fine water spray during operation by free hand. Pulse repetition rate was set in 10 Hz, and the energy intensity varied according to the respective experimental group (200 mJ, 400 mJ or 600 mJ). After the irradiation, the adhesive tape was removed and surfaces were ultrasonically cleaned in 96% isopropanol for 3 minutes. Energy density used was 25.2J/cm^2.

SURFACE ROUGHNESS ANALYSIS

Each ceramic plate was then placed on a glass slide with the treated surface face-up. In order to provide opaque surfaces for optical roughness analysis, the surfaces were gold-sputter coated (E5100, Polaron Equipment Ltd., Hertfordshire, UK) and observed with a confocal microscope (Tandem scanning confocal microscope, Noran Instruments, Middleton, WI, USA). A 546 nm (green) filter in the illumination path acted to reduce chromatic errors, and specimens were viewed via a x100/1.40 NA oil immersion lens and a 4912 monochrome CCD camera (Cohu Inc., San Diego, CA, USA). Using an automatic stage controller (Märzhäuser, Wetzlar-Steindorf, Germany) and image capturing software (AQM 6, Andor Technology, Northern Ireland, UK), the surfaces were optically profiled by sequentially capturing surface images from the highest to the lowest planes of focus, with a step interval of 0.2 µm.

Each captured image stack was then processed (Lucida Analyse, Andor Technology, Northern Ireland, UK) to obtain single images displaying the brightest points in each optical section, whilst still retaining spatial information regarding the location of these points in the original stack. By taking line profiles across these images, roughness profiles were created that were then exported and analyzed in an Excel macro (Andor Technology, Northern Ireland, UK) which determined the roughness. The surface roughness parameter analyzed was the Ra (µm), which means the average roughness, defined as the arithmetic average of the profile ordinates within the measured section (average height).

Ra values were analyzed with Two-way ANOVA. Multiple pairwise comparisons were done with Tukey post-hoc test. In order to meet the requirements of the statistical test, values were transformed into logarithm base 10. Analyses were carried out in the SAS 9.1 statistical package (SAS Institute, Cary, NC, USA) with a 0.05 significance level.

MORPHOLOGICAL EVALUATION

The same gold-sputter coated surfaces were viewed in a scanning electron microscope (SEM / Hitachi S-3500N, Hitachi High-Technologies, Tokyo, Japan). Images from each surface were registered at x100 and x1,000 magnifications. The microscope operated at an accelerating voltage of 15kV with a working distance of between 15 and 27 mm.

Prior to gold coating, surfaces were observed with an optical microscope (x60, EMZ-TR, Meiji Techno Co., Ltd., Tokyo, Japan). Images were registered with a digital camera (Coolpix 990, Nikon, Kingston, UK).

RESULTS

SURFACE ROUGHNESS

Table 1 presents mean values of the surface roughness parameters for the two ceramic systems. The statistical test detected a significant interaction between the main factors (p=0.0006). For the Cercon system, surface treatments resulted in statistically dissimilar Ra values. Surfaces irradiated at 600 mJ presented the highest Ra and control surfaces showed the lowest one. Air abrasion presented Ra values similar to irradiation with 200 mJ and with 400 mJ.

For the Procera Zirconia system, Ra values were higher on laser irradiated surfaces. The irradiation with 600 mJ presented the highest value, followed by 400 mJ and 200 mJ. Air abraded and control surfaces presented similar Ra. Figures 1 and 2 are representative confocal scanning images of each surface treatment / ceramic.

The two ceramic systems presented similar Ra among surfaces irradiated with the same energy intensities of the Er:YAG laser. Procera Zirconia presented a statistically higher Ra than Cercon under the control condition. On the other hand, Cercon presented an increased Ra compared to the other ceramic after air abrasion.

MORPHOLOGICAL EVALUATION

OPTIC MICROSCOPY PREVIOUS TO GOLD-COATING

Figures 3 and 4 are representative optical images of Cercon and Procera Zirconia, respectively. The images clearly indicate the colour alterations caused by Er:YAG irradiation on the two ceramic materials, even when the lower energy intensity was used (Figures 3c and 4c). Higher energy intensities (400 mJ and 600 mJ) caused severe alterations on the zirconia-based materials (Figures 3d-e and 4d-e). The air abraded surfaces did not present significant colour alterations (Figures 3b and 4b).

SCANNING ELECTRON MICROSCOPY (SEM)

The SEM images showed morphologic differences in the ceramic surfaces after the different treatments (Figures 5 and 6). Air abrasion with 50 µm Al_2O_3 particles created a rougher surface compared with the control surfaces for Cercon surfaces but not for the Procera Zirconia ones (Figures 5a-b and 6a-b). Er:YAG laser irradiation caused perceivable loss of material and cracks on the surfaces. The size of these cracks enlarged when the energy intensity increased (Figures 5c-e and 6c-e).

DISCUSSION

The present study was conducted to determine whether Er:YAG irradiation can provide superficial alterations and be used as a surface treatment for Y-TZP ceramics. Surface roughness was measured through confocal scanning microscopy. Although confocal microscopy allows the comprehensive measurement of a sample's surface topography at high resolution (0.2 µm), its use is not as frequent as other techniques like tactile or optical profilometry (17).

The principle effect of laser energy is the conversion of light energy into heat, and the most important interaction between the laser and substrate is the absorption of the laser energy by the substrate (15,16). The pigmentation of the surface and its water content along with other surface characteristics determine the amount of energy that is absorbed by the irradiated surface (16). The absorption of laser energy by Y-TZP ceramics might be compromised since they are water-free materials that present a white and opaque coloration. For this reason, in this study, ceramic plates were coated with graphite to increase the absorption of the Er:YAG laser (7). During preliminary studies, it was noted that laser irradiation promoted minimum or no effects on uncoated surfaces. On the other hand, the effects of Er:YAG laser on surfaces coated by graphite were clearly observed.

Different energy intensities of the Er:YAG laser were tested in this investigation. The results of surface roughness and morphological characterization indicated that irradiation at 600 mJ or 400 mJ is not a viable alternative for surface treatment of Y-TZP ceramics. For both Y-TZP materials tested, high Ra values were noted after irradiation with 600 mJ and 400 mJ. Melting, excessive loss of mass and the presence of some cracks were observed with scanning electron microscopy. The cracks on zirconia surfaces were probably generated during the process of heating and further cooling to ambient temperature. Finally, with optical microscopy, the surface aspects indicated significant colour alterations, possibly caused by an excess of heat, in spite of the constant water cooling during irradiation. These results can be associated with those of a previous investigation, which showed that the optimal etching pattern for a lithium-based ceramic is obtained by low laser power settings, such as 300 mJ (12). The authors stated that higher laser power settings might cause heat damage layers, resulting in over-destruction of the crystal and/or matrix phases (12).

Analysis of the topographic features of surfaces irradiated with 200 mJ demonstrated the mild effect of this energy intensity compared to the other laser settings. Cercon and Procera Zirconia surfaces irradiated with 200 mJ presented higher roughness compared to the respective control surfaces. Some cracks were not as open as the ones observed with the other laser settings, and colour alterations were also detected. No significant loss of structure was observed in the SEM images. These findings share similarities with those of a previous study (7), in which SEM observation of glass-infiltrated alumina irradiated with Nd:YAG laser (100 mJ) demonstrated little material removal, fusing and melting of the most superficial ceramic layer and its posterior re-solidification. According to those authors, this superficial pattern is favorable for the micro-mechanical retention of resin cements (7). Additionally, the findings of the present study demonstrated that for one zirconia system (Cercon), irradiation at 200 mJ provided superficial alterations that resemble those resultant from air abrasion with aluminum oxide particles.

Air abrasion with aluminum oxide particles is a widely recommended surface treatment for high strength ceramics (4). Nevertheless, the results of the present study indicated that the advantages of air abrasion might depend on the Y-TZP material. The air abraded specimens of Procera Zirconia presented similar roughness compared to the control surfaces, while air abraded Cercon surfaces presented increased roughness. Although both ceramics investigated are Y-TZP materials, differences in their manufacturing process and composition might have contributed to these results (5). In an earlier study, the authors observed that air abraded Y-TZP specimens presented inferior surface roughness compared to surface controls. It was suggested that air abrasion reduces surface defects inherent or generated as a result of the manufacturing techniques (8).

The optical penetration depth of Er:YAG lasers is only a few micrometers (16). This characteristic might be advantageous for the surface treatment of dental ceramics since structural modifications would be restricted to the outer surface. Nevertheless, there is limited knowledge regarding the effects of Er:YAG laser irradiation on dental ceramics. The results of the present study clearly indicate that this laser alters the external surfaces of Y-TZP ceramics, and opens a vast range of questions that should be answered through other clinical and in vitro studies. For example, future works might focus on the effects of laser irradiation within the bulk of Y-TZP ceramics to indicate if superficial flaws produced by the irradiation at 200 mJ propagate through the material, and reduce the strength of Y-TZP ceramics after dynamic and cyclic stresses. Finally, the effect of changes in surface topography resultant from laser treatment on the bonding of luting cements, and how long will this bond last in a clinical situation, should be the subject of further investigation

Within the limitations of the present in vitro investigation it can be concluded that irradiation with an Er:YAG laser with high energy intensities is not a reliable surface treatment for Y-TZP ceramics and results in severe alterations to the topography of surfaces. On the other hand, the lower energy intensity (200 mJ) might be a potential method of surface treatment for those ceramics, but further studies are required to confirm this conjecture.

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Table 1 – Mean value (standard deviation) of surface roughness parameters (Ra, µm).

Surface treatment	Cercon Smart Ceramics	Procera Zirconia
Control	0.37 (0.09) Db	0.72 (0.33) Da
Air abrasion	2.41 (0.44) BCa	0.86 (0.19) Db
200 mJ	1.11 (0.21) Ca	1.92 (0.18) Ca
400 mJ	3.92 (0.12) Ba	5.83 (2.91) Ba
600 mJ	13.57 (2.66) Aa	12.05 (3.29) Aa

Means followed by dissimilar letters represent statistically significant differences (Two-way ANOVA/Tukey test, α=0.05). Upper case letters compare surface treatments and low case letters compare ceramic materials.

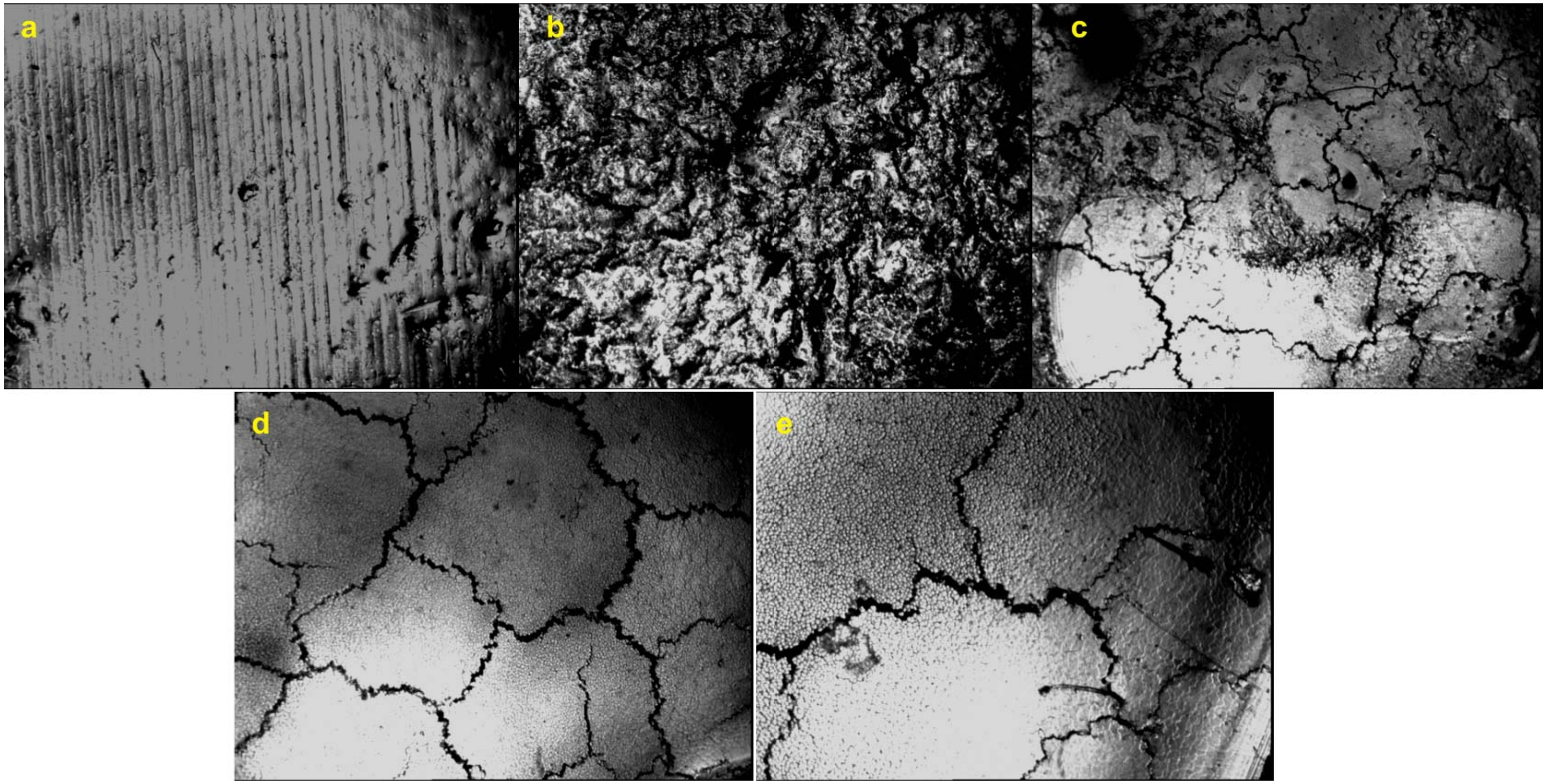

Figure 1 – Confocal scanning images of Cercon ceramic. (a) Control, no superficial treatment, (b) air abrasion, (c) Er:YAG irradiation with 200 mJ energy intensity, (d) Er:YAG irradiation with 400 mJ energy intensity, and (e) Er:YAG irradiation with 600 mJ energy intensity. Tandem scanning confocal microscope (TSM) x100/1.40 NA oil immersion objective. Fieldwidth 100μm.

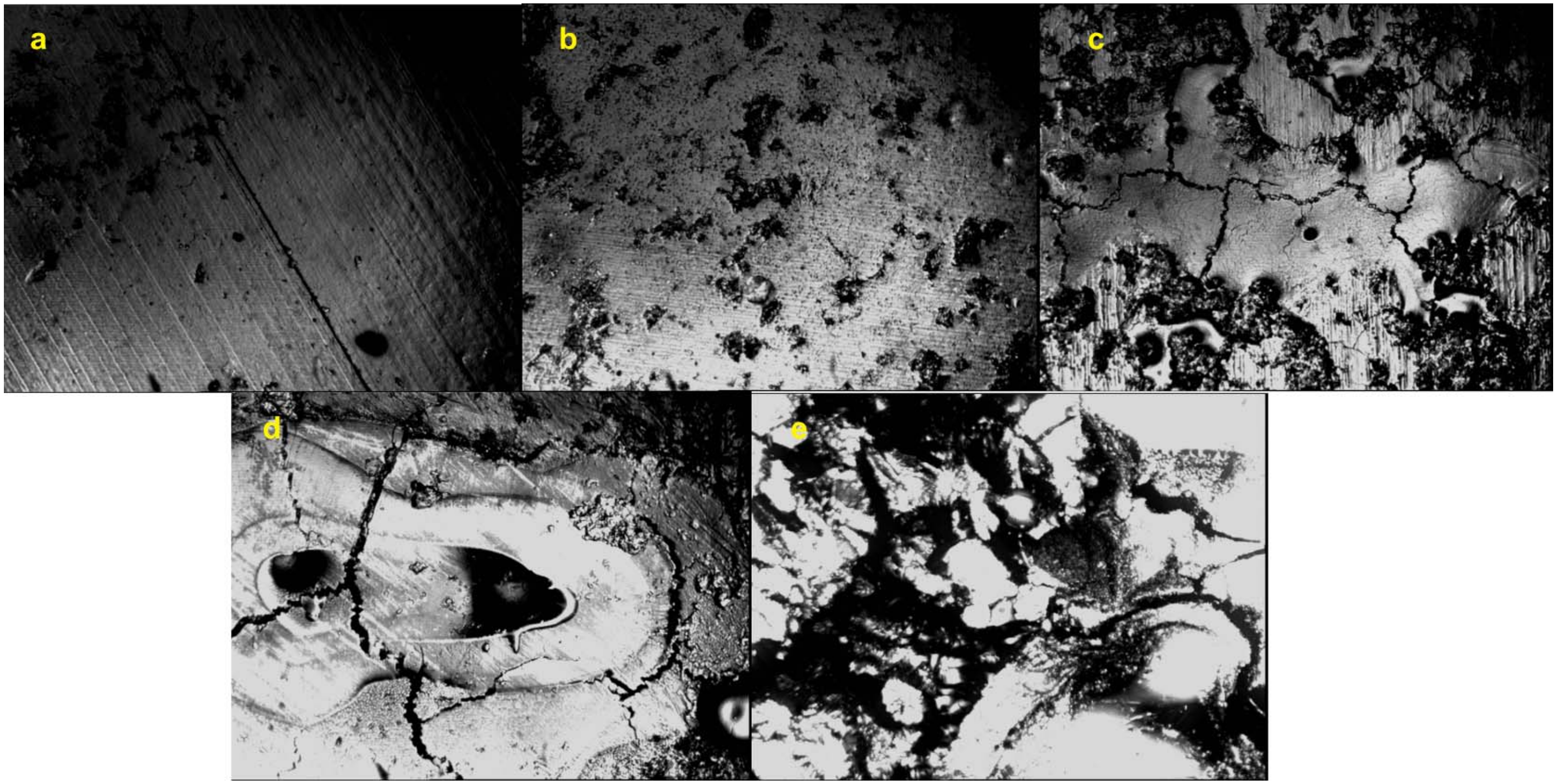

Figure 2 – Confocal scanning images of Procera zirconia ceramic. (a) Control, no superficial treatment, (b) air abrasion, (c) Er:YAG irradiation with 200mJ energy intensity, (d) Er:YAG irradiation with 400mJ energy intensity, and (e) Er:YAG irradiation with 600mJ energy intensity. TSM x100/1.40 NA oil. Fieldwidth 100µm.

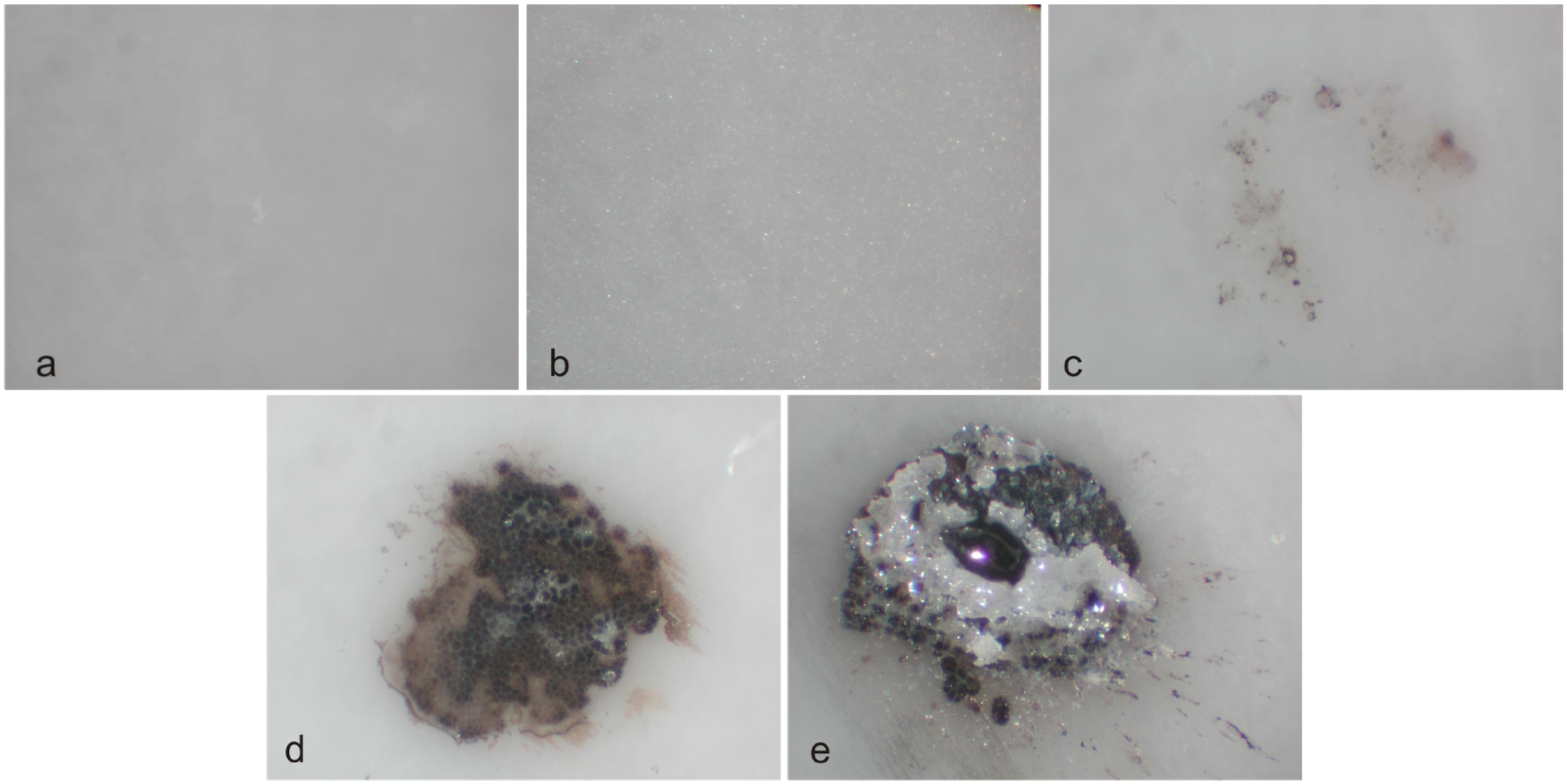

Figure 3 – Optic microscopy images of Cercon surfaces. (a) Control, no superficial treatment, (b) air abrasion, (c) Er:YAG irradiation with 200mJ energy intensity, (d) Er:YAG irradiation with 400mJ energy intensity, and (e) Er:YAG irradiation with 600mJ energy intensity. Original magnification x60. Fieldwidth 2.5 mm.

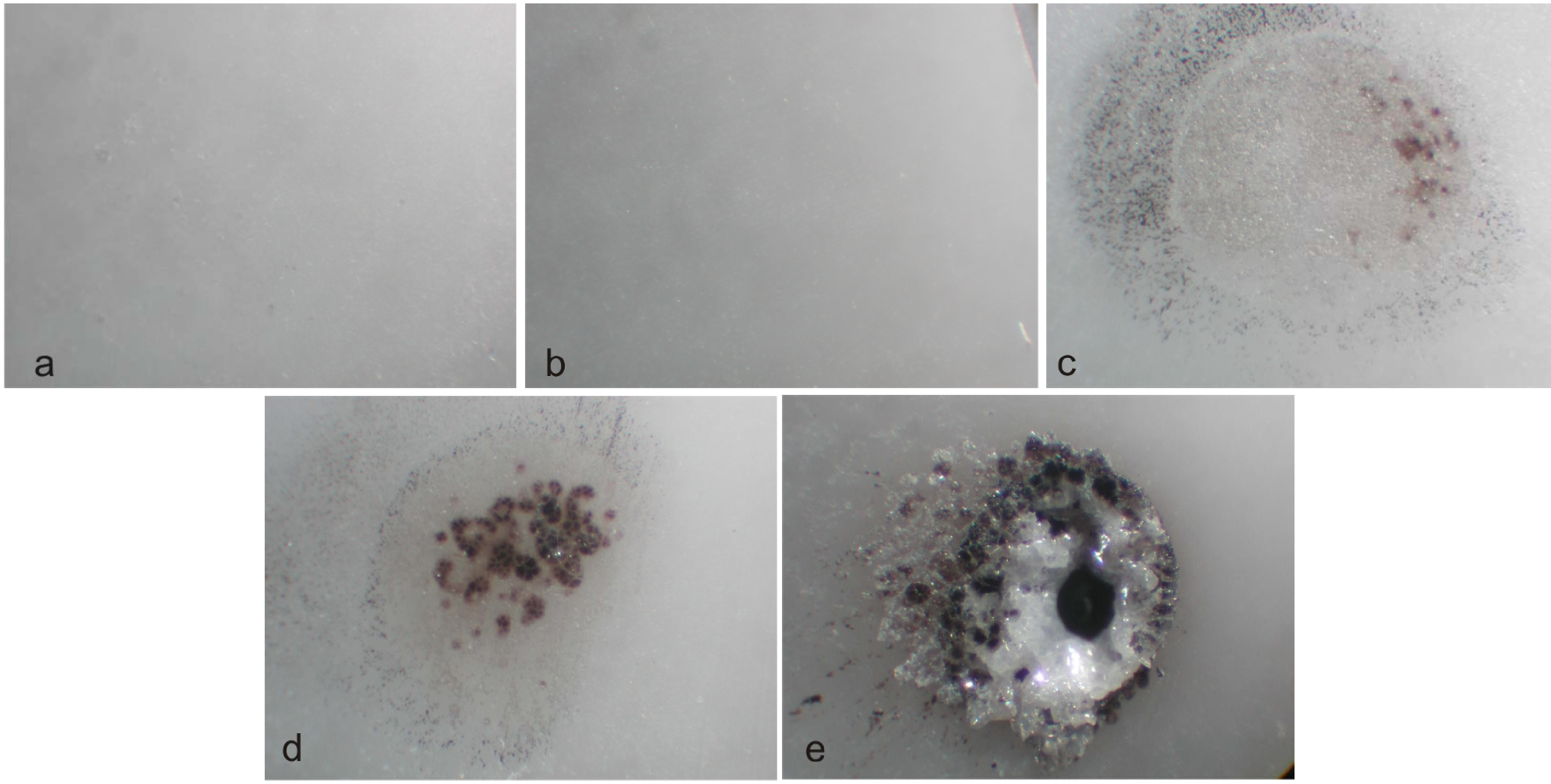

Figure 4 – Optic microscopy images of Procera Zirconia surfaces. (a) Control, no superficial treatment, (b) air abrasion, (c) Er:YAG irradiation with 200mJ energy intensity, (d) Er:YAG irradiation with 400mJ energy intensity, and (e) Er:YAG irradiation with 600mJ energy intensity. Original magnification x60. Fieldwidth 2.5 mm.

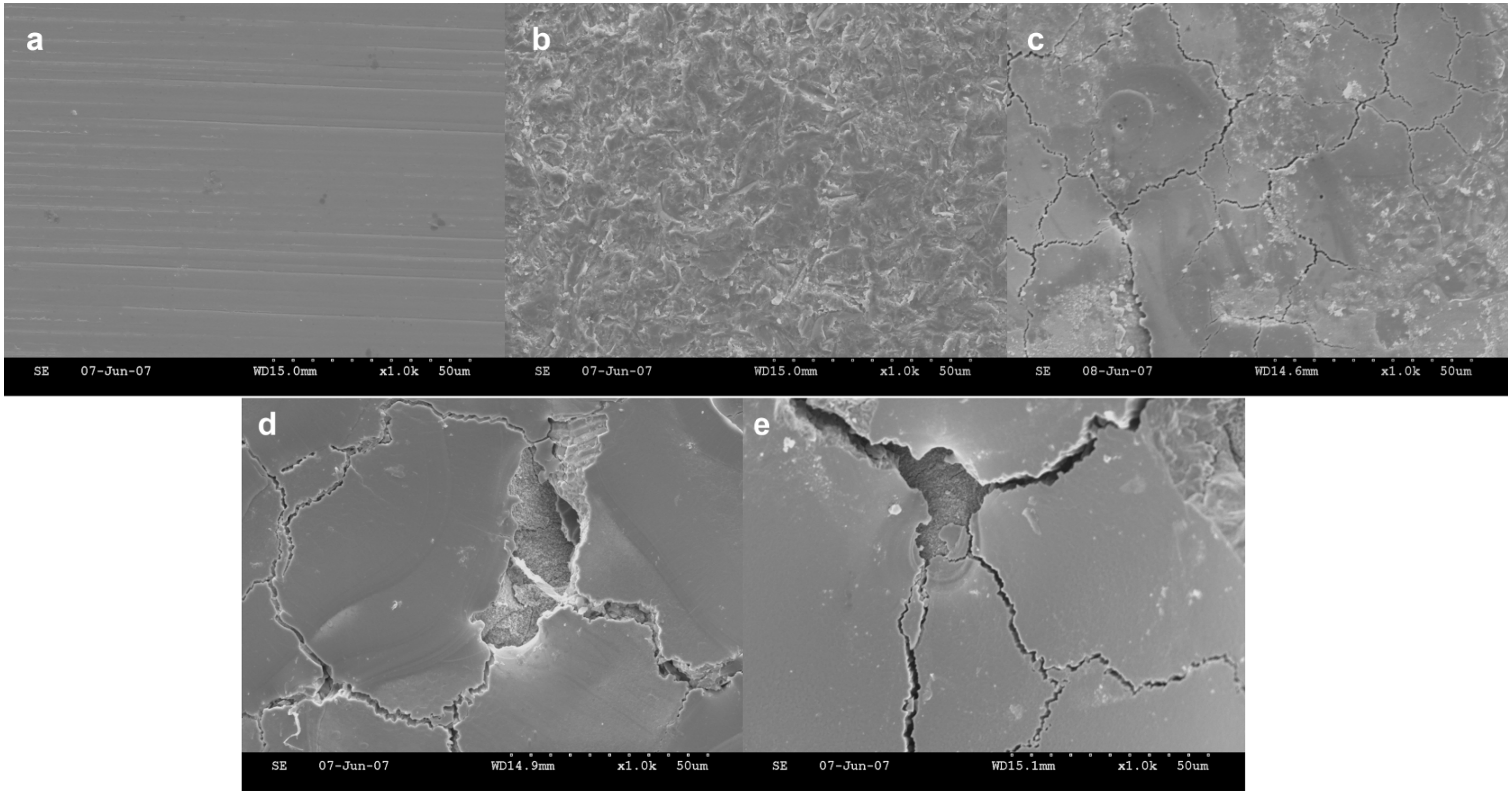

Figure 5 – SEM images of Cercon surfaces. (a) Control, no superficial treatment, (b) air abrasion, (c) Er:YAG irradiation with 200mJ energy intensity, (d) Er:YAG irradiation with 400mJ energy intensity, and (e) Er:YAG irradiation with 600mJ energy intensity. Original magnification x1000.

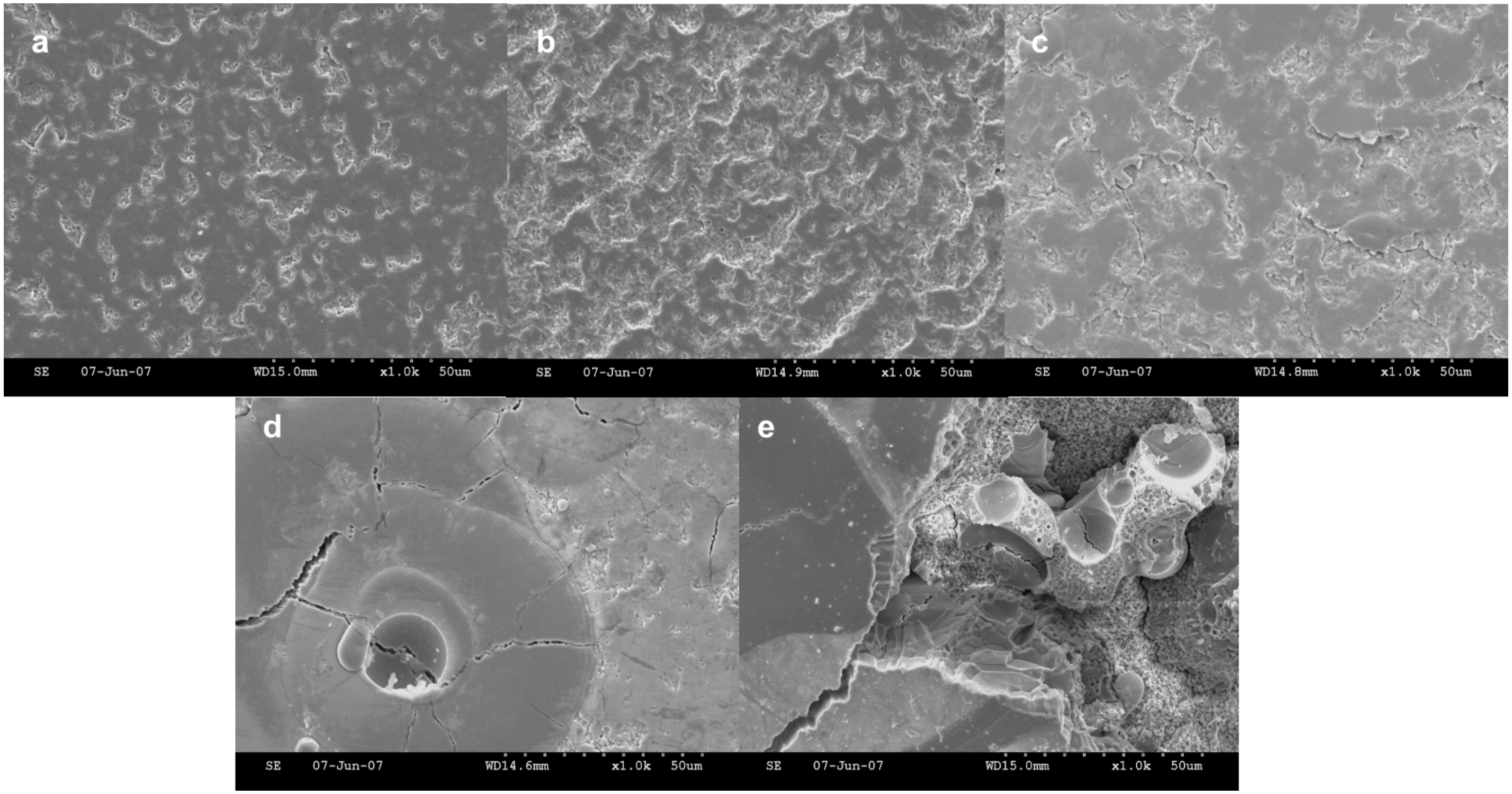

Figure 6 – SEM images of Procera Zirconia surfaces. (a) Control, no superficial treatment, (b) air abrasion, (c) Er:YAG irradiation with 200mJ energy intensity, (d) Er:YAG irradiation with 400mJ energy intensity, and (e) Er:YAG irradiation with 600mJ energy intensity. Original magnification x1000.

CAPÍTULO TRÊS

BOND STRENGTH OF RESIN CEMENTS TO A ZIRCONIA CERAMIC WITH DIFFERENT SURFACE TREATMENTS

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SHORT TITLE: Bond strength to a zirconia ceramic

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ABSTRACT

Objectives: This study evaluated the influence of surface treatments and metal primers on the bond strength of resin cements to an yttrium-stabilized tetragonal zirconia (Y-TZP) ceramic.

Methods: 240 plates of Y-TZP ceramic (Cercon Smart Ceramics) were manufactured (5x3x0.75mm). Plates were randomly assigned into 24 groups (n=10) according to the combination of surface treatment (none, air abrasion with 50µm Al_2O_3 particles, Er:YAG laser irradiation), metal primer (None, Alloy Primer, Metal Primer II, Metaltite), and resin cement (Calibra or Panavia F2.0). Fragments of dentin, trimmed into a cylindrical shape (0.8mm diameter), were fixed to ceramic surfaces with the resin cements. The micro-shear bond test was carried out at a 1mm/min speed until failure, and ceramic surfaces were examined with a stereoscopic microscope after debonding. Bond strengths were analyzed through 3-Way ANOVA/Tukey test, with a 5% significance level. Changes in topography after surface treatments were evaluated with scanning electron microscopy.

Results: Surface treatments significantly modified the topography of the Y-TZP ceramic. Air abrasion resulted in increased bond strength for both resin cements. However, air abraded and laser irradiated specimens presented higher bond strength with Calibra resin cement than with Panavia F2.0. Both resin cements presented similar behaviour on untreated surfaces. The three metal primers yielded an increase in bond strength, resulting in similar results regardless of the surface treatment and resin cement. Irrespective of the experimental group, adhesive failures were the most prevalent.

Significance: Air abrasion with 50µm Al_2O_3 particles and the application of metal primers increased bond strength to Y-TZP surfaces for both resin cements tested.

KEYWORDS: zirconia, resin cement, air abrasion, laser, metal primer, bond strength.

INTRODUCTION

The evolution of yttrium stabilized tetragonal zirconia (Y-TZP) materials has introduced a new class of dental ceramics to the market [1]. Although Y-TZP has been used as a ceramic biomaterial in medical applications since the late sixties, its use in dentistry is relatively recent, and occurred following advances in CAD-CAM (computer-aided design/manufacturing) technology [1-4]. These high-strength materials offer a wide variety of clinical applications, such as orthodontic brackets, posts, implant abutments and frameworks for crowns and bridges [5,6].

Zirconia materials differ from other high strength dental ceramics because of their distinct mechanism of stress-induced transformation toughening, which means that the material undergoes microstructural changes when submitted to stress [2,4]. Y-TZP ceramics can actively resist crack propagation through a transformation from a tetragonal to a monoclinic phase at the tip of a crack, which is accompanied by a volume increase [2]. The mechanical properties of Y-TZP materials such as flexural and fracture resistance are considerably higher than those of other dental ceramics [4]. The flexural resistance of Y-TZP ceramics can reach values from 700 to 1200 MPa [7,8]. These values exceed the maximal occlusal loads during normal chewing [8]. Y-TZP materials might also exhibit fracture resistance higher than 2,000 N, which is almost twice the value obtained for alumina-based materials and at least three times the value demonstrated by lithium disilicate-based ceramics [9].

Although improved mechanical properties are important for the long-term performance of a ceramic material, the clinical success of fixed ceramic prostheses seems to be strongly dependent on the cementation procedure. There is a common thought that conventional methods of adhesive cementation, which include prior acid etching of the ceramic surface with hydrofluoric acid and further silanation are not efficient for Y-TZP ceramics because of their lack of silica and glass phase [1,3,11]. Even though some Y-TZP manufacturers suggest the use of air abrasion or tribochemical coating previously to adhesive cementation, the effect of those surface treatments on the mechanical properties of Y-TZP materials is controversial, and both positive and negative results have been described in the literature [12,13]. Therefore, the most appropriate surface treatment for Y-

TZP ceramics still has to be determined. Some studies have suggested the use of Er:YAG (erbium-doped yttrium aluminium garnet) laser to enhance the bond strength of adhesive materials to composite resins used for indirect restorations, and lithia-based ceramics [14,15]. However, the capacity of the Er:YAG laser to increase the roughness of Y-TZP ceramics for adhesive luting procedures has not been investigated.

There is some evidence that improved bonding to Y-TZP ceramics might be achieved using materials with a chemical affinity for metal oxides [1,5,11,16,17]. Phosphate ester monomers, such as MDP (10-methacryloyloxyi-decyl-dihyidrogenphosphate), chemically react with the zirconium dioxide, promoting a water-resistant bond to densely sintered zirconia ceramic [11]. Phosphate ester monomers can be present in both resin cements and adhesive systems. In addition, special adhesive monomers for improving bonding to metal alloys have been developed and their effects on adhesive bonding to Y-TZP ceramics should be evaluated. These metal primers contain MDP and other monomers like VBATDT (6-(4-vinylbenzyl-n-propyl)amino-1,3,5-triazine-2,4-dithione), MEPS (thiophosphoric methacrylate) and MTU-6 (6-methacryloyloxyhexyl-2-thiouracil-5-carboxylate) [18,19].

Despite the increase in the clinical use of zirconia ceramics, further evidence regarding the adhesive cementation of Y-TZP restorations is necessary to establish the most reliable technique [10]. There are still some possibilities for improving bonding to Y-TZP ceramics to be tested, including modern techniques for surface treatments and adhesive primer materials. Therefore, the purpose of this study was to evaluate the effect of different metal primers and surface treatment methods on the bond strength of two resin cements to a Y-TZP ceramic. The null hypotheses tested were that surface treatments as well as metal primer application do not influence bond strengths to Y-TZP ceramic regardless of the type of resin cement used (MDP-based and Bis-GMA-based).

MATERIAL AND METHODS

In the present study, 40 recently extracted non-carious human third molars were used to obtain cylindrical dentin specimens. Teeth were gathered after the approval of the Commission for Ethics of Piracicaba Dental School (#108/2006) and stored in 0.1% thymol solution for less than 6 months after extraction. Dentin slices of 3.5-mm thickness were obtained by removing the root portion and the occlusal enamel surface of each tooth. Dentin slices were polished with silicon carbide papers under water to remove remnants of enamel over the dentin surface and to standardize the smear layer. Slices were sectioned in the "x" and "y" axis, which resulted in six sticks with a 2 x 2 x 3.5-mm dimension. Sticks were placed in a specimen former device and trimmed with fine diamond burs (FG507, Kerr Diamond Blu White Burs, Kerr Corporation, Orange, CA, USA) in a high-speed hand piece with constant water-cooling. After trimming, the fragments had a cylindrical extremity with a height of 1.3 mm and a diameter of 0.8 mm. Two hundred and forty dentin specimens were obtained in this manner and stored in distilled water at 37oC. Figure 1 describes the preparation of dentin specimens.

Two hundred and forty plates with a dimension of 5x3x0.75-mm were obtained from a 94% ZrO_2 stabilized by 5% Y_2O_3 ceramic (Cercon Smart Ceramics, Degudent, Hanau, Germany, batch number 20015645). The two hundred and forty ceramic plates and the same number of trimmed dentin specimens were randomly allocated into twenty-four experimental groups (n=10), according to the combination of surface treatment (none, air abrasion or Er:YAG laser irradiation), metal primer (none, Alloy Primer, Metal Primer II or Metaltite) and resin cement [Bis-GMA-based (Calibra) or MDP-based (Panavia F2.0)]. Table 1 presents the composition of the restorative materials used in this study.

The two hundred and forty Y-TZP plates were distributed in three groups (n=80) and submitted to one of the following surface treatments: none (control), air abrasion or laser irradiation. In the air abraded and lased groups, the superficial area to be further treated (1.76mm^2) was delimitated with adhesive tape. Surface treatments were performed as follow:

- Surface treatment control: specimens were only ultrasonically cleaned with 96% isopropanol for 3 minutes.
- Air abrasion: Air abrasion was performed with 53µm aluminium oxide particles (Aquacut, Medivance Instruments Ltd. London, UK) at a 2.5 bar pressure for 15 seconds at a distance of 10mm and perpendicular to the surface. Then, the adhesive tape was removed and the plates were ultrasonically cleaned with 96% isopropanol for 3 minutes.

- Er:YAG laser irradiation: Surfaces were coated with graphite prior to the laser irradiation to increase the energy absorption. The laser equipment used was an Er:YAG laser (OPUS 20 Er:YAG / CO2 Dental Laser Surgical System, Sharplan Medical Systems, Yokneam, Israel) emitting a 2.94 µm wavelength. A 1,000-µm-diameter straight-type contact probe was used perpendicular to the surface. Surfaces were lased for 5 seconds using a fine water spray. The pulse repetition rate was set at 10 Hz, and the energy intensity at 200 mJ. After irradiation, the adhesive tape was removed and surfaces were ultrasonically cleaned in 96% isopropanol for 3 minutes.

The eighty ceramic plates from each surface treatment group were divided into four subgroups (n=20): no coating (control), Alloy Primer, Metal Primer II or Metaltite. The respective metal primer was applied in a thin coat and left undisturbed for 60 seconds. Following the respective surface treatment and metal primer application, the twenty plates were divided into two groups (n=10) according to the resin cement used: MDP-based resin cement (Panavia F2.0) or Bis-GMA-based resin cement (Calibra Esthetic Resin Cement). The dentin specimens were cemented onto the ceramic plates with the following recommendations.

- Panavia F2.0:

Equal amounts of ED Primer II A&B were mixed and applied to the dentin cylinder. After 30 seconds, the adhesive layer was gently air dried. Equal amounts of paste A&B were dispensed and mixed for 20 seconds. The mixture of the paste was applied to the surface and excess cement was removed with a dental explorer. Margins were light cured for 20 seconds per surface, and oxygen-blocking gel (Oxyguard II) was applied for 3 minutes and then washed with air-water spray.

- Calibra Esthetic Resin Cement:

One drop of Prime & Bond NT adhesive and another of Self-Cure Activator were placed into a clean plastic mixing well. The content was mixed for 2 seconds with a clean, unused brush tip. Immediately, the mixed adhesive/activator was applied to thoroughly wet the dentin surface. After 20 seconds, the excess solvent was removed by gently drying with clean, dry air from a dental syringe for 5 seconds. The mixed adhesive/activator was light cured for 10 seconds.

A single coat of mixed adhesive/activator was applied to the internal bonding surface of the restoration and air dried for 5 seconds. Equal amounts of Calibra Esthetic Resin Cement base paste and catalyst paste (Regular viscosity) were mixed for 20 seconds. A uniform and thin layer of cement was applied on the ceramic plate with a dental explorer. The dentin specimen was seat with gradual pressure. Gross excess was removed from marginal areas with the dental explorer. All marginal areas were light cured for 20 seconds from each direction.

During the restorative procedures, the light output of the light-curing unit (Optilux VCL 401, Demetron Research Co., Danbury, CT, USA) was measured with a radiometer (Demetron Research Co., Danbury, CT, USA) and was greater than 660mW/cm2. Specimens were stored in distilled water at 37oC for 24 hours. After 24h, excess resin cement and adhesive were removed using razor blades under an optical microscope (x45, SDZ-PL, Kyowa Optical Co., Tokyo, Japan).

Each ceramic plate with its dentin specimen was fixed to a micro-shear device adapted to a miniature load testing machine (SMAC LAL95, SMAC Europe, Horshan, Sussek, UK) with cyanoacrylate glue (SuperGlue, Loctite, Henkel Loctite, Hertfordshire, UK). A thin wire (0,2 mm thickness) was looped around the dentin cylindrical extremity, and the shear force was applied at a cross-head speed of 1mm/min until debonding (Figure 1g). KgF values were converted in MPa. After debonding, the fractured surfaces were evaluated with an optical microscope (x100 magnification) to classify the failure modes into one of the following categories: (A) adhesive failure at the interface between the ceramic and resin luting agent or between the resin luting agent and the dentin interface; (C) cohesive failure within the ceramic, within the resin luting agent, or within the dentin only; and (M) adhesive and cohesive failure at the same site, or a mixed failure.

Bond strength data were statistically analyzed by three-way ANOVA, with the main factors resin cement, surface treatment and metal primer. All possible interactions were included in the model. Multiple pairwise comparisons were done with the Tukey test. Statistical analysis was carried out in SAS 9.1 (SAS Institute, Cary, NC, USA) with a significance level of 5%.

Six additional Y-TZP plates were examined using scanning electron microscopy to evaluate changes in the ceramic topography after the surface treatments. Ceramic plates (n=2, for each surface treatment group) were treated and cleaned as described previously. Then, they were placed in a metallic stub keeping the treated surface face-up. Surfaces were gold-sputter coated (E5100, Polaron Equipment Ltd., Hertfordshire, UK) and viewed in a scanning electron microscope (SEM / Hitachi S-3500N, Hitachi High-Technologies, Tokyo, Japan). The microscope operated at an accelerating voltage of 15kV with a working distance of between 15 and 27mm.

RESULTS

Table 2 shows the bond strength results. A significant statistical interaction between resin cements and surface treatments was detected (p=0.004). Therefore, the association between these two main factors was similar in the four levels of the factor metal primer. A significant difference was also noted in the factor metal primer (p<0.01) and the three solutions increased the bond strength to a similar extent, regardless of the resin cement and surface treatment.

With the surface treated groups (air abrasion and Er:YAG laser irradiation), Calibra resin cement had higher bond strength than Panavia F2.0 resin cement. Both materials presented similar bond strength when no surface treatment was used. With the groups cemented with Panavia F2.0, air abrasion resulted in significantly higher bond strengths; while laser irradiation and the absence of surface treatment presented similar results. In the groups luted with Calibra, there was a significant difference between all the surface treatments; air abrasion promoted the highest mean bond strength followed by Er:YAG laser irradiation and no surface treatment.

Table 3 describes the distribution of failure modes in the groups cemented with Panavia F 2.0 and Calibra, respectively. Adhesive failures were the most prevalent in the 24 experimental groups, with an average of 78% adhesive failures between ceramic and resin luting agent or between the resin luting agent and the dentin interface, and 22% mixed failures. No cohesive failure of the substrates (ceramic, resin cement or dentin) was observed.

SEM images show the morphologic differences among the Y-TZP plates after the surface treatments (Figure 2). Air abrasion with 50µm Al_2O_3 particles (Figure 2b) created a rougher surface compared with the control surface and Er:YAG laser irradiation (Figures 2a and 2c). Er:YAG laser irradiation originated a smooth surface, with some perceivable cracks (asterisks).

DISCUSSION

Previous studies have evaluated the bond strength of adhesive restorative materials to Y-TZP ceramics. Shear and tensile bond strength tests were the methods most frequently used in those investigations [1,3,5,6,10,11,16,17,20,21]. In both methods, specimens had only one adhesive interface to be tested, i.e. between ceramic and resin cement. However, in the clinical situation, both the interfaces between ceramic and adhesive restorative material and between the adhesive restorative material and tooth structure are present Thus, the performance of the complex tooth structure – restorative material – Y-TZP ceramic unit must be investigated. During the preliminary investigations for the present study, Y-TZP plates were luted to dentin surfaces and specimens were sectioned for the microtensile bond strength test. The incidence of premature failures during sectioning was very high (almost 100%), yielding unreliable results. The long period necessary to section the densely sintered Y-TZP ceramics seems to weaken the adhesive interface, resulting in the premature failures. To overcome this limitation and to test both interfaces, a modification of the shear bond strength test was performed in the present study. The micro-shear test was conducted using cylindrically trimmed dentin specimens luted onto Y-TZP plates (Figure 1), instead of the conventional micro-shear method [22].

The surface treatments investigated in this study resulted in significantly different bond strengths. Moreover, SEM images demonstrated considerable qualitative differences in the surface topography of Y-TZP plates after the surface treatments. Images showed that air abrasion appears to be a more efficient method to modify zirconia surfaces compared with laser irradiation using the parameters set for this study. This finding can be directly related to bond strength results, which showed that both resin cements yielded higher bond strengths after air abrasion. Some investigations also indicated that superior bonding to zirconia is obtained when surfaces are air abraded [5,6]. Air abraded surfaces might present an increased surface area, which favors wettability. However, some authors have stated that the microporosities created by surface treatments may act as crack initiators, weakening ceramic materials [13,20]. Thus, the effect of those alterations on the durability of Y-TZP restorations should be investigated in long term clinical trials to determine whether the higher retention of air abraded surfaces compensates for the changes in mechanical properties.

In the present study, irradiation of Y-TZP surfaces with Er:YAG laser was proposed as a surface treatment method. The Er:YAG laser has the ability to remove particles by micro explosions and by vaporization, a process called ablation. During laser treatment, local temperature changes due to heating and cooling phases create internal tensions that can damage the material [15]. The mechanical properties of Y-TZP ceramics can be negatively affected by changes in temperature, which can induce phase transformation [12]. Therefore, in this study, a lower power setting for the Er:YAG laser was selected in accordance to the results of a preliminary investigation (200 mJ) and surfaces were lased with constant water cooling. Bond strength results indicated that laser irradiation was not as effective in improving bond strength as air abrasion, for both resin cements. When Panavia F2.0 was used, lased treated and untreated surfaces presented similar results. The manufacturer of the MDP-based material does not recommend the application of a layer of adhesive system on the ceramic surface, which is in contrast to the instructions of the Bis-GMA based resin cement. Since the MDP-based resin cement was applied directly to the laser irradiated ceramic, both the slight surface modification provided by the Er:YAG laser and the lack of contact between resin cement and surface might have contributed to bond strengths that were similar to the untreated surfaces. On the other hand, when Calibra was used, the bond strengths of the lased surfaces were superior to those of the untreated surfaces, thus, the better wettability of the adhesive system applied to the Y-TZP surface prior to the resin cement might have compensated for the limited surface modification promoted by the laser irradiation.

Metal primers were developed as an alternative approach to promote a durable bond to noble metal alloys [19,23]. The VBATDT monomer, a thione-thiol tautomer, was the first product introduced as a coupling agent between methacrylate-based monomers and noble metal alloys [24]. The coupling mechanism of this monomer has been assigned to the transformation of thione to thiol groups on noble metal surface, subsequently primary bond formation and to the copolymerization of vinyl groups with the methacrylate-based resin monomer [23]. The metal primers investigated in the present study are vinyl-thione coupling agents with different functional monomers. Besides their different compositions, the bond strength results indicated a similar performance for the three systems, significantly strengthening the bond to the Y-TZP ceramic for both resin cements. This finding might suggest that vinyl-thione coupling agents also present a chemical affinity to zirconia surfaces. Previously, it was stated that the application of a MDP-containing bonding / silane coupling agent is the key factor for a reliable resin bond to a Y-TZP ceramic and is not influenced by the resin luting agent [3]. The bonding / silane agent improves the wettability of the air abraded zirconia surface. Although a different ceramic material was investigated in the present study, the effect of the metal primers might have been similar, which is increasing the surface wettability of resin cements.

In contrast with the results of some previous studies, which have shown that the chemical affinity between MDP-based material and Y-TZP ceramic creates a strong bond, able to resist thermal aging and water storage [1,5,11], in the present study, the MDP-based resin cement did not present higher bond strength to Y-TZP surfaces compared with the Bis-GMA-based material. Both cements showed similar results only on untreated surfaces, while in the air abraded and laser irradiated surfaces, the Bis-GMA-based resin cement showed significantly stronger bonding. A previous investigation observed that air abrading zirconia surfaces resulted in immediate high bond strength to a conventional dual-curing Bis-GMA resin composite, which was reduced to zero after long-term storage and thermal cycling in distilled water [11]. Another study also stated that the bonding of Bis-GMA composites to zirconia is not resistant to thermal aging [1]. In the present study, only the immediate bond strength (measured 24h after the polymerization of the resin cements) was tested. Since a water exposure period of only 24h is insufficient to permit diffusion of water into the adhesive interface, it should be considered that different results might have been found if specimens were submitted to an aging protocol. Therefore, further in vitro studies with longer storage periods should be performed to determine the long-term durability of the bond.

The failure mode results indicated that, regardless of the experimental group, most failures of the complex tooth structure – resin cement – Y-TZP ceramic were adhesive, which left the zirconia plates free of remnants of adhesive materials. This finding might suggest that even when a higher bond strength to zirconia is obtained, this bond is not as strong as the adhesion between dentin and restorative material.

CONCLUSION

Within the limitations of this in vitro study, it can be concluded that metal primers and air abrasion with 50μm Al_2O_3 particles can have a synergic effect on the dentin bonding to Y-TZP ceramics. The Bis-GMA-based resin cement presented a stronger immediate bond on treated surfaces than the MDP-based material.

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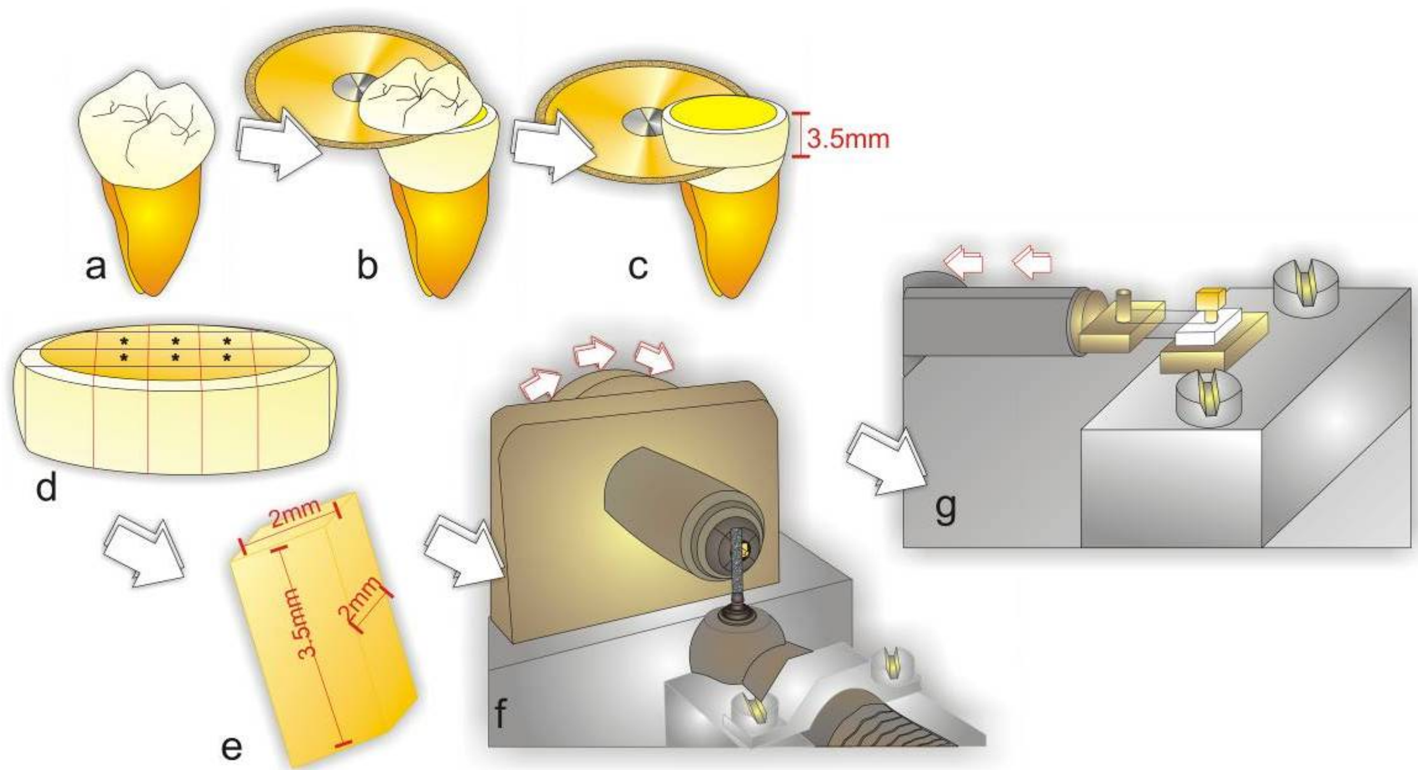

Figure 1 – Schematic design of dentin specimen preparation. (a) Human third molar; (b) Section of enamel occlusal surfaces; (c) Section of the 3.5-mm thick dentin slice; (d) Dentin slice sectioned in the "x" and "y" axis. Dots represent the six dentin sticks selected per tooth (e) Dentin stick with 2x2x3.5-mm dimension; (f) Dentin stick trimmed in the specimen former device; (g) Specimen fixed to the miniature load testing machine for the micro-shear testing. Arrows represent the direction of the movement of the arm.

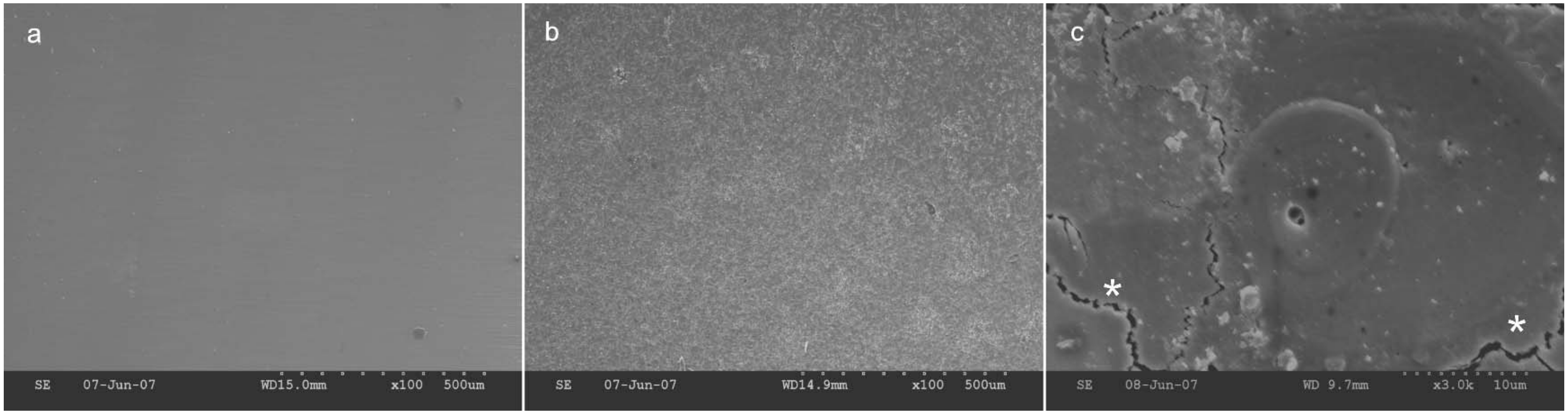

Figure 2 – SEM images (original magnification x500) of ceramic surfaces. (a) Y-TZP surface untreated (control); (b) Y-TZP surface treated air abrasion with 53µm Al_2O_3 particles; (c) Y-TZP surface irradiated with the Er:YAG laser. Asterisks represent cracks caused by laser irradiation.

Table 1 – Description of materials used in this study with their manufactures', batch number, classification, and composition.

Material, Manufacturer, Batch n.		Composition
Panavia F2.0, Kuraray Medical Inc., Okayama, Japan, 51185	ED Primer II	Solution A: HEMA, 10-MDP, 5-NMSA, water, accelerators. Solution B: 5-NMSA, water, initiators, accelerators
	Panavia F2.0	Paste A: 10-MDP, hydrophobic aromatic DMA, hydrophobic aliphatic DMA, hydrophilic aliphatic DMA, silanated silica filler, silanated colloidal silica, dl-Camphorquinone, initiators. Paste B: hydrophobic aromatic DMA, hydrophobic aliphatic DMA, hydrophilic aliphatic DMA, silanated barium glass filler, sodium fluoride, initiators, accelerators, pigments
Calibra Esthetic Resin Cement, Dentsply-Caulk, Milford, DE, USA	Conditioner	34% phosphoric acid, silica, water
	Prime & Bond NT + Ativador	Adhesive: di- and trimethacrylate resins, PENTA, photoinitiators, stabilizers, nanofillers, amorphous silicone dioxide, cetylamine hydrofluoride, acetone. Activator: TPBSS, acetone, ethanol
	Calibra	Base: DMA resins; Bis-GMA, camphorquinone; stabilizers, glass fillers, fumed silica; titanium dioxide, pigments. Catalyst: DMA resins; Bis-GMA, catalyst; stabilizers, glass fillers, fumed silica
Alloy Primer, Kuraray Medical Inc., 224AE		VBATDT; 10-MDP, acetone
Metal Primer II, GC Corporation, Tokyo, Japan, 0612073		MEPS
Metaltite, Tokuyama Dental Corporation, Tokyo, Japan, 020BM1		MTU-6, ethanol

HEMA=2-hydroxyethyl methacrylate; 10-MDP=10-Methacryloyloxydecyl dihydrogen phosphate; 5-NMSA= N-Methacryloyl-5-aminosalicylic acid; DMA= dimethacrylate; PENTA: dipentaerythritol penta acrylate monophosphate Bis-GMA: bisphenol A diglycidylether methacrylate TPBSS= aromatic sodium sulfinate; VBATDT=6-(4-vinylbenzyl-n-propyl)amino-1,3,5-triazine-2,4-dithione; MEPS= thiophosphoric methacrylate; MTU-6=6-methacryloyloxyhexyl 2-thiouracil-5-carboxylate.

Table 2 – Mean (standard-deviation) of the micro-shear bond strength in MPa.

Metal primer	Resin Cement	Surface Treatment			
		None	Air abrasion	Er:YAG laser	
None	**Panavia**	17.0 (3.5) Ab n=10	22.3 (5.2) Ba n=10	15.8 (3.5) Bb n=8	♣
	Calibra	16.6 (2.1) Ac n=9	24.3 (3.0) Aa n=7	23.0 (4.1) Ab n=8	
Alloy Primer	**Panavia**	20.4 (4.6) Ab n=9	24.2 (2.5) Ba n=8	19.6 (1.5) Bb n=10	♦
	Calibra	21.0 (3.3) Ac n=9	26.6 (2.4) Aa n=10	20.7 (6.4) Ab n=7	
Metal Primer II	**Panavia**	21.8 (3.0) Ab n=9	26.1 (3.9) Ba n=9	19.8 (3.2) Bb n=9	♦
	Calibra	21.60 (3.67) Ac n=8	27.99 (4.48) Aa n=9	22.72 (5.28) Ab n=8	
Metaltite	**Panavia**	20.6 (5.2) Ab n=7	24.3 (3.9) Ba n=9	19.3 (3.2) Bb n=9	♦
	Calibra	20.7 (3.4) Ac n=7	26.5 (3.5) Aa n=8	23.0 (3.0) Ab n=8	

Coefficient of variation = 15.75%

Same letters are not statistically different (Three-way ANOVA/Tukey test, α=0.05). Upper case letters compare resin cements within surface treatment/metal primer. Lower case letters compare surface treatments within resin cement/metal primer. Symbols (♣ ♦) represent differences between metal primers.

Table 3 – Percentage of the failure modes in each experimental group.

Resin Cement	Metal primer	Surface Treatment					
		None		Air abrasion		Er:YAG laser	
		A	M	A	M	A	M
Panavia	**None**	70	30	71	29	78	22
	Alloy Primer	75	25	75	25	71	29
	Metal Primer II	70	30	67	33	75	25
	Metaltite	78	22	70	30	86	14
Calibra	**None**	80	20	100	0	100	0
	Alloy Primer	60	40	75	25	100	0
	Metal Primer II	75	25	86	14	88	13
	Metaltite	70	30	83	17	71	29

A=Adhesive

M=Mixed

4. CONCLUSÕES

Com base nos resultados obtidos e dentro das limitações dos presentes experimentos pode-se concluir que:

- A irradiação de cerâmicas Y-TZP com altas intensidades de energia do laser de Er:YAG (400mJ e 600mJ) é um protocolo excessivamente agressivo, resultando em severas alterações na topografia das superfícies.

- Os efeitos da irradiação com 200 mJ de intensidade de energia são mais brandos que as demais intensidades de energia do laser de Er:YAG. Dependendo do material Y-TZP, este protocolo pode promover maior ou menor rugosidade superficial comparado ao jateamento com partículas de óxido de alumínio.

- A aplicação de primers para metais e o jateamento com partículas de óxido de alumínio podem ter efeito sinérgico no aumento da resistência de união à cerâmica Y-TZP.

- O cimento resinoso a base de Bis-GMA apresenta resistência de união imediata mais forte em superfícies abrasionadas ou irradiadas com laser de Er:YAG comparado ao cimento a base de MDP.

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* De acordo com a norma da UNICAMP/FOP, baseada na norma do International Committee of Medical Journal Editors – Grupo de Vancouver. Abreviatura dos periódicos em conformidade com Medline.

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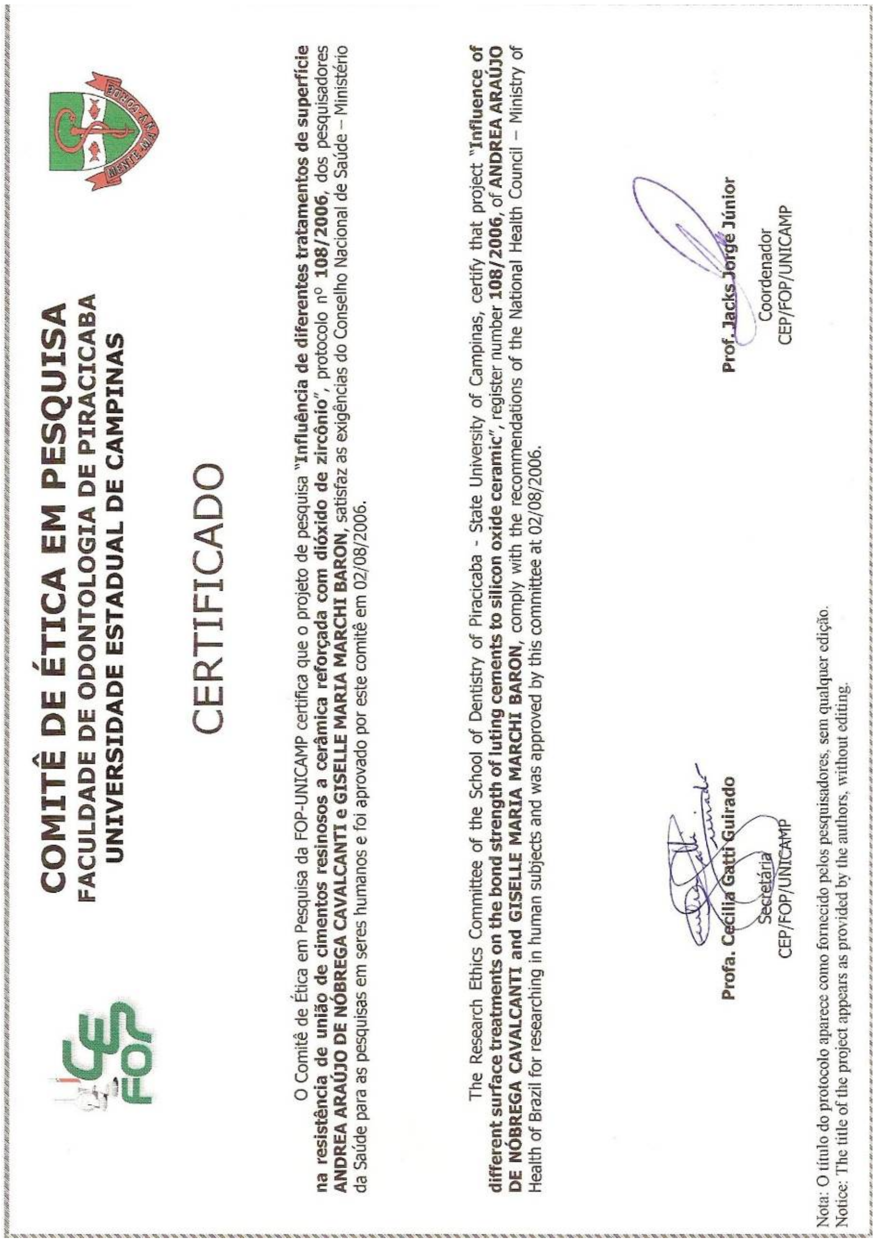
6. ANEXO

6.1. CERTIFICADO DO COMITÊ DE ÉTICA EM PESQUISA, FOP-UNICAMP



COMITÊ DE ÉTICA EM PESQUISA
FACULDADE DE ODONTOLOGIA DE PIRACICABA
UNIVERSIDADE ESTADUAL DE CAMPINAS

CERTIFICADO

O Comitê de Ética em Pesquisa da FOP-UNICAMP certifica que o projeto de pesquisa **"Influência de diferentes tratamentos de superfície na resistência de união de cimentos resinosos a cerâmica reforçada com dióxido de zircônio"**, protocolo nº **108/2006**, dos pesquisadores **ANDREA ARAÚJO DE NÓBREGA CAVALCANTI e GISELLE MARIA MARCHI BARON**, satisfaz as exigências do Conselho Nacional de Saúde – Ministério da Saúde para as pesquisas em seres humanos e foi aprovado por este comitê em 02/08/2006.

The Research Ethics Committee of the School of Dentistry of Piracicaba - State University of Campinas, certify that project **"Influence of different surface treatments on the bond strength of luting cements to silicon oxide ceramic"**, register number **108/2006**, of **ANDREA ARAÚJO DE NÓBREGA CAVALCANTI and GISELLE MARIA MARCHI BARON**, comply with the recommendations of the National Health Council – Ministry of Health of Brazil for researching in human subjects and was approved by this committee at 02/08/2006.

Profa. Cecilia Gatti Guirado
Secretária
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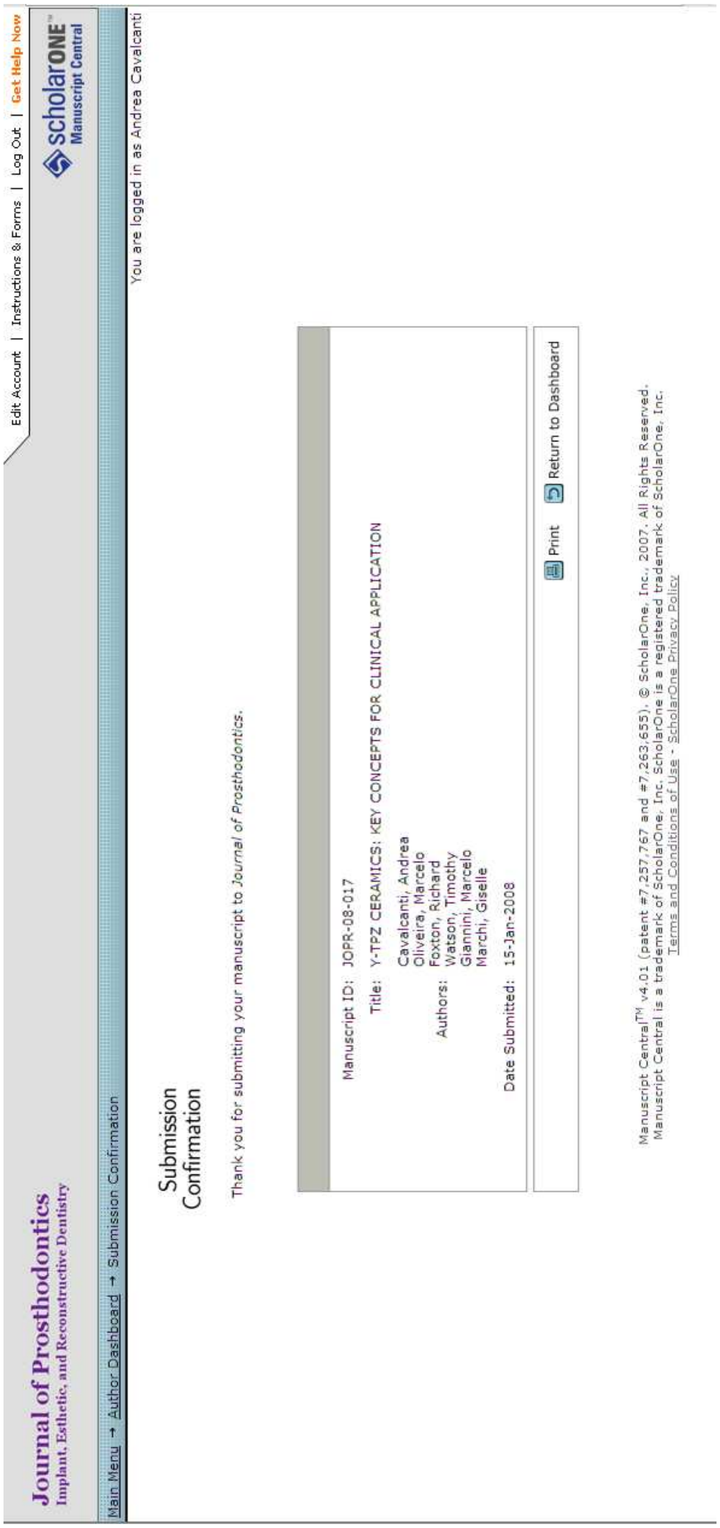
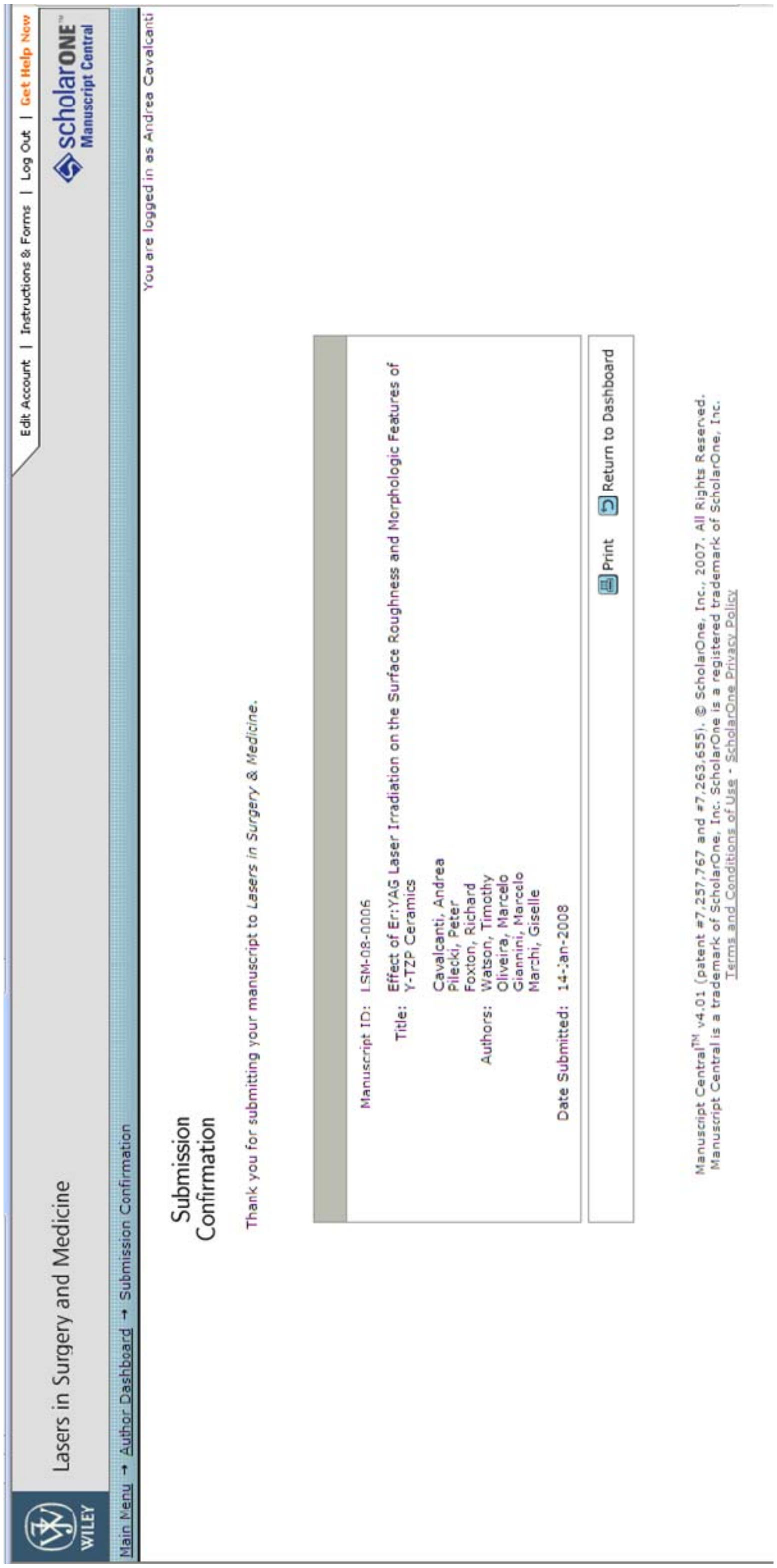
Nota: O título do protocolo aparece como fornecido pelos pesquisadores, sem qualquer edição.
Notice: The title of the project appears as provided by the authors, without editing.

6.2. COMPROVAÇÃO DA SUBMISSÃO DO ARTIGO REFERENTE AO CAPÍTULO 1.



6.3. COMPROVAÇÃO DA SUBMISSÃO DO ARTIGO REFERENTE AO CAPÍTULO 2.



6.4. COMPROVAÇÃO DA SUBMISSÃO DO ARTIGO REFERENTE AO CAPÍTULO 3.