UNIVERSIDADE ESTADUAL PAULISTA
"JÚLIO DE MESQUITA FILHO"
Campus de São José dos Campos
Instituto de Ciência e Tecnologia

HILTON RIQUIERI

IMPACTO DO PROCESSO DE CRISTALIZAÇÃO NA MICROESTRUTURA E NA RESISTÊNCIA À FLEXÃO DE CERÂMICAS DE SILICATO DE LÍTIO REFORÇADAS POR ZIRCÔNIA

2017

HILTON RIQUIERI

IMPACTO DO PROCESSO DE CRISTALIZAÇÃO NA MICROESTRUTURA E NA RESISTÊNCIA À FLEXÃO DE CERÂMICAS DE SILICATO DE LÍTIO REFORÇADAS POR ZIRCÔNIA

Tese apresentada ao Instituto de Ciência e Tecnologia, Universidade Estadual Paulista (Unesp), Campus de São José dos Campos, como parte dos requisitos para obtenção do título de DOUTOR, pelo Programa de Pós-Graduação em ODONTOLOGIA RESTAURADORA, Área de Odontologia Restauradora, Especialidade em Prótese Dentária.

Orientadora: Prof. Dr. Guilherme de Siqueira Ferreira Anzaloni Saavedra

São José dos Campos

2017

Instituto de Ciência e Tecnologia [internet]. Normalização de tese e dissertação [acesso em 2018]. Disponível em http://www.ict.unesp.br/biblioteca/normalizacao

Apresentação gráfica e normalização de acordo com as normas estabelecidas pelo Serviço de Normalização de Documentos da Seção Técnica de Referência e Atendimento ao Usuário e Documentação (STRAUD).

Riquieri, Hilton
Impacto do processo de cristalização na microestrutura e na resistência à flexão de cerâmicas de silicato de lítio reforçadas por zircônia / Hilton Riquieri. - São José dos Campos : [s.n.], 2017.
52 f. : il.

Tese (Doutorado em Odontologia Restauradora) - Pós-Graduação em Odontologia Restauradora - Universidade Estadual Paulista (Unesp), Instituto de Ciência e Tecnologia, São José dos Campos, 2017.
Orientador: Guilherme Siqueira Ferreira Anzaloni Saavedra
Coorientador: Renata Marques Melo Marinho

1. Cerâmicas. 2. Vitrocerâmicas. 3. Resistência de materiais. 4. Silicato de Lítio reforçado por Zircônia. I. Siqueira Ferreira Anzaloni Saavedra, Guilherme, orient. II. Marques Melo Marinho, Renata, coorient. III. Universidade Estadual Paulista (Unesp), Instituto de Ciência e Tecnologia, São José dos Campos. IV. Universidade Estadual Paulista 'Júlio de Mesquita Filho' - Unesp. V. Universidade Estadual Paulista (Unesp). VI. Título.

Ficha catalográfica elaborada pela Biblioteca Profa Leila Novaes - Seção Técnica de Aquisição e Tratamento da Informação (STATI) do ICT/UNESP. Dados fornecidos pelo autor
Ana Paula Mattozo Durante CRB8/6141

BANCA EXAMINADORA

Prof. Dr. Guilherme de Siqueira Ferreira Anzaloni Saavedra (Orientador)
Universidade Estadual Paulista
Instituto de Ciência e Tecnologia
São José dos Campos

Profa. Dra. Pesquisadora Renata Marques de Melo Marinho
Universidade Estadual Paulista
Instituto de Ciência e Tecnologia
São José dos Campos

Prof. Dr. Alexandre Luiz Souto Borges
Universidade Estadual Paulista
Instituto de Ciência e Tecnologia
São José dos Campos

Dr. Tiago Moreira Bastos Campos
Instituto Tecnológico da Aeronáutica
Centro Técnico Aeroespacial
São José dos Campos

Prof. Dr. Marcelo Lucchesi Teixeira
Faculdade de Odontologia São Leopoldo Mandic
Departamento de Prótese Dentária
Campinas

São José dos Campos, 04 de Dezembro de 2017.

DEDICATÓRIA

À ***Debora***, minha amada esposa, companheira de alegrias e dificuldades, por entender minhas ausências, minhas viagens a cursos e congressos. Você faz a diferença!

Aos meus filhos ***Rodrigo***, ***Breno***, ***Arthur*** e ***Enrico***. Vocês são a minha força. Essa obra é o resultado do esforço de todos!

Aos meus pais, ***José*** (i*n memorian*) e ***Divina***, responsáveis pelo sólido embasamento que me deu a sustentação necessária para superar os mais difíceis obstáculos. Uma vida terá se passado e ainda assim faltarão palavras para expressar o quanto sou grato!

Aos meus sogros, ***Júlia*** e ***Luís.*** Nada disso seria possível sem o suporte oferecido por vocês dois durante esse tempo em que voltei a ser Aluno, amenizando minha ausência junto à filha, e sendo fundamentais na criação e educação dos netos.

A ***Regina***, ***Carlos***, ***Eurípedes*** e ***Aparecida***, meus irmãos, pela memória afetiva e por estarem sempre presentes em minha vida, apesar da distância.

AGRADECIMENTOS

Sempre que estamos concluindo algo grande em nossa vida, paramos para avaliar como foi a nossa jornada. Ao final deste projeto de pesquisa, claramente percebo que não sou mais o mesmo. Cresci muito nesses três anos, e acho importante deixar a minha gratidão àqueles que participaram desse meu crescimento:

À minha adorada Família, que aceitaram com resignação mais um sacrifício para que eu pudesse correr em busca dos meus sonhos.

Ao meu Orientador, Professor **Dr. Guilherme de Siqueira Ferreira Anzaloni** Saavedra, que acreditou no meu potencial e me trouxe até aqui, não só pela amizade fortalecida durante essa instigante jornada. A decisão de encarar mais esse desafio tem tudo a ver com sua incessante procura pelas respostas. Uma verdadeira bússola em direção ao saber. Certamente, se sou um profissional melhor hoje, muito devo ao seu perfeccionismo e empenho absoluto na busca pelas respostas

À minha Co-orientadora, Professora Pesquisadora **Dra. Renata Marques de Melo Marinho**, pelo essencial apoio e atenção desde o início desse projeto.

Ao Professor **Dr. Marco Antônio Bottino**, por todas as oportunidades que se abriram à minha frente após conhecê-lo e por todo o crescimento pessoal e profissional que só estando próximo a uma pessoa com sua experiência pode proporcionar.

Aos técnicos do Laboratório de Pesquisas de Materiais, **Marcos Vestali**, pela ajuda e pela sempre presente solicitude, e, de forma especial, à **Dra. Thaís Paradella**, pelas brilhantes imagens obtidas.

Ao **Dr. Tiago Moreira Bastos Campos**, por acompanhar o trabalho de pesquisa na parte mais desafiadora e ajudar a elucidar, de forma simples, as mais intrigantes dúvidas. Sua ajuda foi fundamental para a execução desse trabalho.

Aos amigos das turmas de 2015 e 2016, com quem tive o prazer de conviver: **Alexandre Alonso**, **Aline Barcellos**, **Aline Firmino**, **Aline Lins**, **Amanda dal Piva**, **Bruna Lucatto**, **Carlos Datte**, **Dayana Campanelli**, **Dominique Toyama**, **Eliseo Chun**, **Fabrício Monteiro**, **Fernanda Abu-Izze**, **Gabriela Nishioka**, **Jean Miranda**, **Jéssica Dias**, **João Paulo Tribst**, **Marcelo Oliani**, **Lígia Yamamoto**, **Patrícia Claudio**, **Pedro Prado**, **Polyanna Nogueira**, **Rodrigo Diniz**, **Stefhany Astuti**, **Tabata Sato**, **Vinícius Anéas**....e de forma especial a **Gabriela Freitas Ramos**, **Julio Nogueira Luz**, **Karen Archangelo**, **Nayara Barchetta**, **Larissa Alves** e **Nathália Ramos**, que em muito contribuíram para diminuir minhas dificuldades durante as aulas e trabalhos dos créditos.....e, de uma maneira mais que especial, à **Jaiane Bandoli Monteiro,** batalhadora incansável; sua determinação em perseguir seus objetivos só é superada pelo desprendimento, demonstrado nos momentos em que, mesmo já bastante atarefada, ainda assim se colocava à disposição para ajudar.

Aos professores: **Dr. Renato Sussumu Nishioka**, **Dr. Alexandre Luiz Souto Borges**, **Dr. Rubens Nisie Tango** e **Dr. Eduardo Bresciani**. Nobre missão é a deles de conduzir os alunos.

À Universidade Estadual Paulista "Júlio de Mesquita Filho" – Instituto de Ciência e Tecnologia de São José dos Campos - Unesp, através do seu Diretor **Prof. Estevão Tomomitsu Kimpara** e Vice-Diretora **Prof.a Adjunta Rebeca di Nicoló**.

Ao programa de Pós graduação em Odontologia Restauradora, coordenado pela **Prof.a Titular Marcia Carneiro Valera**.

À Seção Técnica de Pós-Graduação nas pessoas de
Rosemary Salgado, **Ivan Damasceno** e **Bruno Tanaka**.

A todos aqueles que, de forma direta ou indireta, dispuseram de um pouco de seu tempo para estender a mão. Desde cedo aprendi que sozinhos não vamos longe, por isso peço desculpas se me esqueci de alguém dentre as inúmeras pessoas de alma elevada que, de uma maneira ou outra, ajudaram-me a enfrentar e a superar mais esse desafio.

Agradeço também às pedras no caminho, sem elas não há como se transformar em coisa melhor. Passar por elas nos fortalece.

E por fim, à força maior, **Deus**, alicerce e fonte de inspiração durante o caminho.
Obrigado a todos!

"Tudo é uma questão de manter a mente quieta, a espinha ereta e o coração tranquilo". Walter Franco

SUMÁRIO

Riquieri H. Impacto do processo de cristalização na microestrutura e na resistência à flexão de cerâmicas de silicato de lítio reforçadas por zircônia [tese]. São José dos Campos (SP): Universidade Estadual Paulista (Unesp), Instituto de Ciência e Tecnologia; 2017.

RESUMO

O objetivo deste trabalho foi avaliar o silicato de lítio reforçado por zircônia quanto a sua microestrutura e as mesmas propriedades mecânicas em diferentes fases de cristalização. Cento e vinte amostras de discos de silicato de lítio reforçado por zircônia foram usinados de acordo com as normas ISO 6872 (12x1,2mm) para o ensaio de flexão biaxial. Foram separados em 4 grupos de acordo com a fase de cristalização. Grupo I: 30 amostras de Celtra pré cristalizado (CNC); Grupo II: 30 amostras de Celtra cristalizado (CC); Grupo III: 30 amostras de Suprinity Não Cristalizado (SNC) e Grupo IV: 30 amostras de Suprinity Cristalizado (SC). Os corpos de prova foram submetidos ao ensaio mecânico de flexão biaxial e em seguida realizadas análises qualitativas e quantitativas. Por meio microscopia eletrônica de varredura, microscopia eletrônica com emissão de campo MEV-FEG, EDS e difração de raios X (n=4), foi realizada a caracterização completa dos materiais e análise morfológica da microestrutura para todos os grupos. Para as análises estatísticas foram utilizados o módulo Weibull (m) e resistência característica (σ_0).

Palavras-chave: Cerâmicas, Vitrocerâmicas, Resistência de materiais, Silicato de Lítio Reforçado por Zircônia.

Riquieri H. Impact of crystallization firing process on the microstructure and flexural strength of zirconia-reinforced lithium silicate glass-ceramics [doctorate thesis]. São José dos Campos (SP): São Paulo State University (Unesp), Institute of Science and Technology; 2017.

ABSTRACT

The objective of this work was to evaluate the lithium silicate reinforced by zirconia as to its microstructure and the same mechanical properties in different phases of crystallization. One hundred and twenty samples of zirconia-reinforced lithium silicate discs were machined according to ISO 6872 (12x1,2mm) standards for the biaxial flexural test. They were separated into 4 groups according to the crystallization step. Group I: 30 samples of Pre-Crystallized Celtra (CPC); Group II: 30 samples of Crystallized Celtra (CC); Group III: 30 samples of Uncrystallized Suprinity (SNC) and Group IV: 30 samples of Crystallized Suprinity (SC). The specimens were submitted to the mechanical biaxial flexion test and qualitative and quantitative analyzes were performed. Scanning Electron Microscopy, Electron Microscopy with Field emission SEM-FEG, EDS and X-ray diffraction (n = 4) were carried out to characterize the materials and morphological analysis of the microstructure for all groups. The Weibull (m) and characteristic resistance (σ0) were used for the statistical analysis.

Keywords: Ceramics. Vitroceramics. Resistance of Materials. Zirconia Reinforced Lithium Silicate.

1 INTRODUÇÃO

Os materiais cerâmicos odontológicos são usados em tratamentos reabilitadores por apresentarem biocompatibilidade, estética e propriedades mecânicas (Albakry et al., 2003). Essas propriedades aliadas às propriedades ópticas as tornam similares às estruturas dentárias (Mainjot et al., 2016).

Cerâmicas que já são consagradas para uso clínico devido às suas excelentes propriedades ópticas e resistência mecânica são à base de dissilicato de lítio, dada a possibilidade de uma série de aplicações clínicas, como laminados, restaurações do tipo inlay e onlay, coroas parciais e coroas totais unitárias anteriores e posteriores (Zarone et al., 2016). É um material confiável o suficiente para ser usado em espessuras de até 0,5 mm e proporciona restaurações mais duradouras do que aquelas feitas de infraestrutura de zircônia recobertas com porcelana (Guess et al., 2010; Silva et al., 2012).

A apresentação comercial é em forma de pastilhas para injeção ou blocos para usinagem em CAD/CAM (Computer Aided Design/Computer Aided Manufacture), sendo que os blocos também apresentam um estado intermediário de cristalização que necessitam de tratamento térmico para o crescimento dos metassilicatos de lítio, os quais evoluem e formam os cristais de dissilicato de lítio, aumentando a resistência à flexão e à fratura (Lien et al., 2015).

A busca constante por materiais restauradores totalmente cerâmicos que associem estética e resistência contribuiu para o desenvolvimento de vitro-cerâmicas, como aquelas à base de silicato de lítio reforçado com zircônia (Vita Zahnfabrik, 2014) e são indicadas para restaurações tipo

inlays, onlays, coroas totais anteriores, coroas totais posteriores e prótese implanto suportada (Elsaka, Elnaghy, 2016).

A matriz vítrea das vitro-cerâmicas é bastante susceptível à propagação de trincas (Borba et al., 2011) e para melhorar este aspecto, materiais de menor módulo de elasticidade podem ser incorporados na matriz cerâmica (Mark, 1996; Petrini et al., 2013). As empresas Vita Zahnfabrik e Dentsply anunciaram que o conteúdo de dióxido de zircônio incorporado é dez vezes maior se comparada as outras vitro-cerâmicas (Vita Zahnfabrik, 2014; Dentsply – DeguDent GmbH, 2014). Este conteúdo está disposto de forma homogênea e com pequeno tamanho de grãos, o que acarretaria alta resistência e excelente polimento superficial (Traini et al., 2016).

No que diz respeito à cristalização, os blocos em CAD/CAM apresentam um estado intermediário, que depois de fresados, ainda necessitam de tratamento térmico para crescimento dos cristais de silicato de lítio. Este fato se torna imprescindível pois não causa alterações na fase cristalina do material, o que parece não modificar a microestrutura cerâmica original (Aurélio et al., 2017).

A introdução da fase de cristalização em cerâmicas vítreas tem como principal intenção criar mecanismos de tenacificação que aumentam sua tolerância ao dano (Lohbauer et al., 2010). Assim, a microestrutura do material tem relação direta com sua tenacidade à fratura (K_{IC}), pois expressa sua capacidade de resistir à propagação da trinca. As fraturas das cerâmicas ocorrem quando o fator de intensidade de tensão na ponta da trinca (K_I) atinge um valor crítico (K_{IC}) (Quinn, 2007).

As cerâmicas com alto conteúdo de matriz vítrea mostraram-se susceptíveis à degradação por fadiga, estimulando o desenvolvimento de novos materiais para suprir essa deficiência (Belli et al., 2017). Desse modo, a incorporação de óxido de zircônio resultou no aumento da

resistência mecânica, melhorando polimento superficial. Além disso, conter partículas de zircônia em sua matriz, trata-se de uma cerâmica vítrea cuja superfície pode ser condicionada com ácido fluorídrico (Sato et al., 2016).

O silicato de lítio pode se apresentar em um estado de pré-processamento e pronto para o uso. Também são totalmente produzidas em ambiente industrial ideal, permitindo um alto padrão de qualidade em nível laboratorial, deixando de ser manual/aditivo para ser mecanizado/subtrativo (Rinke et al., 2015). Esses materiais são oferecidos em um estágio meta-cristalizado para facilitar a usinagem e para alcançar os ideais de cor só depois passar pela queima de cristalização final (Belli et al., 2017).

Diante do exposto, por serem novos materiais e adequados a uma tecnologia que ganha cada vez mais espaço, há a necessidade de se conhecer o comportamento biomecânico e as características microestruturais das diferentes formas de apresentação concernente à cristalização desses novos materiais, onde um dos fabricantes recomenda o uso do material não só na forma cristalizada, mas também na forma parcialmente cristalizada.

2 ARTIGO

2.1 Artigo – Riquieri H, Monteiro J, Viegas DC, Campos TMB, Melo RM, Saavedra GSFA. Impacto do processo de cristalização na microestrutura e na resistência à flexão de cerâmicas de silicato de lítio reforçadas por zircônia / *Impact of crystallization firing process on the microstructure and flexural strength of zirconia-reinforced lithium silicate glass-ceramics*

RESUMO

O objetivo deste estudo foi caracterizar a microestrutura de duas cerâmicas de silicatos de lítio reforçadas com zircônia com resina em diferentes estágios de cristalização e avaliar suas propriedades mecânicas antes e depois do tratamento térmico.
Métodos: MEV-FEG e EDS foram realizados para caracterização microestrutural. Para avaliar o padrão de cristalização da cerâmica e a composição molecular, utilizou-se DRX. A dureza de Vickers, a resistência à fratura pelo método de indução e a resistência à flexão também foram medidas. Foram produzidos cento e quarenta discos cerâmicos (12 mm de diâmetro e 1,2 mm de espessura) e alocados em quatro grupos (n = 30), de acordo com dois fatores: material cerâmico (Vita Suprinity e Celtra Duo) e estádios de cristalização (parcialmente cristalizados e cristalizados) . Os espécimes foram testados em água para a determinação dos parâmetros de Weibull.
Resultados: CC apresentou maior resistência característica (251,25 MPa) e dureza (693,333 ± 10,85 GPa). Por outro lado, o SPC revelou a menor resistência característica (106,95 MPa), apresentou dureza significativamente menor (597,533 ± 33,97 GPa). De acordo com o módulo Weibull, o SPC revelou uma maior probabilidade de falha (m = 7.07), enquanto SC é o menor (m = 5,38). A FEG-SEM mostrou que é necessário realizar o tratamento térmico em cerâmicas parcialmente cristalizadas para cristalização em zircônia. SC mostra menor teor de zircônia cristalizada do que CC. A análise fractográfica mostrou a origem da fratura em um defeito crítico inicial, com ondas de propagação de energia direcionadas

transversalmente ao estresse de tração principal.
Conclusão: o tratamento térmico tem uma influência direta sobre a resistência à flexão e a microestrutura de cerâmica de silicato de lítio reforçada com zircônia com resina.

Palavras-chave: Materiais dentários. Cerâmica dental. Fabricação assistida por computador. Resistência à flexão biaxial.

ABSTRACT

The objective of this study was to characterize the microstructure of two resin-bonded zirconia-reinforced lithium silicates ceramics in different crystallization stages and evaluate their mechanical properties before and after the thermal treatment.
Methods: SEM-FEG and EDS were performed for microstructural characterization. For evaluation of the pattern of crystallization of the ceramics and the molecular composition, XRD was used. Vickers hardness, fracture toughness by indentation method and flexural strength were also measured. One hundred and forty ceramic discs were produced (12mm diameter and 1.2mm thick) and allocated into four groups (n = 30), according to two factors: ceramic material (Vita Suprinity and Celtra Duo) and crystallization stages (partially crystallized and crystallized). The specimens were further tested in water for determination of Weibull parameters.
Results: CC showed higher characteristic strength (251.25 MPa) and hardness (693.333 ± 10.85 GPa). On the other hand, PCS revealed the lowest characteristic strength (106.95 MPa), had significantly mildest hardness (597.533 ± 33.97 GPa). According to the Weibull modulus, PCS revealed a higher probability of failure (m = 7.07) while CS the lowest (m = 5.38). FEG-SEM showed that it is necessary to perform the heat treatment in partially crystallized ceramics for crystallization to zirconia. CS shows lower content of crystallized zirconia than CC. The fractographic analysis showed the origin of the fracture in an initial critical defect, with energy propagation waves directed transversely to the main tensile stress.
Conclusion: The heat treatment has a direct influence on the flexural strength and microstructure of resin-bonded zirconia-reinforced lithium silicate ceramics.

Keywords: Dental Materials. Dental ceramics. Computer-aided manufacturing. Biaxial flexural strength.

Introduction

Ceramic materials in dentistry are widely used to rehabilitation treatments (such as teeth replacement) by presenting biocompatibility and good mechanical properties (Albakry et al., 2003). Besides, the mimetic ability of their optical properties makes this material similar to tooth structure (D'Arcangelo et al., 2016; Mainjot et al., 2016). The constant search for all-ceramic restorative materials that unite aesthetic and strength contributed to development of glass-ceramics (i.e., zirconia reinforced lithium silicate glass-ceramics) by the companies Vita and Dentsply in conjunction with the Fraunhofer Institute for Silicate Research (Germany), and marketed separately under different product brands, i.e., Vita Suprinity (VITA) and Celtra Duo (Dentsply) (Belli et al., 2017; Wendler et al., 2017). Both ZLS glass-ceramics are recommended to inlays, onlays, full-contour anterior and posterior crowns, and also implant-supported prosthesis (Rinke et al., 2015; Elsaka e Elnaghy, 2016).

The glassy matrix of vitreous ceramics is quite susceptible to crack propagation (Borba et al., 2011), and to degradation under fatigue loads (Belli et al., 2017). In this sense, reinforced microstructures have been purposed to make up those deficiencies and get ceramic materials even more better (Belli et al., 2017). The manufacturers announced that the zirconia dioxide content incorporated in ZLS ceramic materials is ten times higher when compared to other glass-ceramic materials (Vita Zahnfabrik, 2014; Dentsply, 2014). This compound is homogeneously arranged and has small grains, which could result in higher resistance, and also better superficial polishing (Traini et al., 2016). Even with dioxide zirconia on its glass matrix, ZLS glass-ceramic materials belong to a class of sensitive acid ceramics, and it means that their surface can be etched by hydrofluoric acid (Sato et al., 2016).

ZLS glass-ceramics are marketed in a pre-processing state, available as pre-fabricated ceramic blocks, which allow less internal flaws and bubbles and a high quality and reliability of ceramic restorations produced by these blocks in a mechanized/subtractive way (Rinke et al., 2015). To make easier the machining process, ZLS glass-ceramics are available in a meta-sintered stage (intermediate), and only after a heat treatment, on which the lithium silicate will grow up, the ceramic gets the final color and strength (D'Arcangelo et al., 2016; Belli et al., 2017). The crystallization process is essential because it do not change the crystalline phase of ceramic material, what seems do not change the original ZLS microstructure (Aurélio et al., 2017). Also, the introduction of this crystallization phase in vitreous ceramics has as main intention to create toughness mechanisms, that will increase its damage tolerance (Lohbauer et al., 2017), since the microstructure has a direct relation with the fracture toughness (K_{IC}), expressing the material's ability to resist the crack propagation (Quinn, 2007).

Given the aforementioned concepts, and taking into account that ZLS glass-ceramics are a relatively new material, developed for a technology which is gaining more and more space in dentistry, there is a great interesting of the scientific community about the biomechanical behavior and microstructure characteristics of the different ZLS ceramic available concerning the heat treatment (D'Arcangelo et al., 2016). In this sense, the present study evaluated the microstructure of zirconia-reinforced lithium silicate glass-ceramics in a state partial or fully crystallized, and also the mechanical properties of these ceramic materials before and after the crystallization process. The null hypotheses tested was that the ZLS glass-ceramics would have the same mechanical properties and microstructural characteristics before and after the heat treatment.

Materials and methods

Two zirconia-reinforced lithium disilicate ceramic materials (Vita Suprinity - VITA Zahnfabrik H. Rauter GmbH & Co., Bad Säckingen, Germany, lote 49270, and Celtra Duo - Degudent GmbH, Hanau, Wolfgang, Germany, lote 18018171) were used to produce one hundred and forty ceramic discs. The specimens were divided into two test conditions (no crystallization firing process; with crystallization firing process).

2.1 Specimens preparation

The ceramic blocks were machined in a conventional lathe (Nardini, Americana, São Paulo, Brazil) in order to get cylinders (final diameter: 12 mm). The cylinders were cut by a precision cutting machine (Isomet 1000, Buehler, Lake Bluff, Illinois, USA) in discs with the final thickness of 1.2 mm.

The ceramic specimens were randomly separately, and a half of both ceramic materials was submitted to a crystallization cycle in a specific oven for each ZLS ceramic (Vita Vacumat 6000MP, Vita Zahnfabrik, Bad Säckingen, Alemanha; Multimat, DentslySirona, Hanau, Alemanha), according to temperature recommendations provided by the manufacturers (Table 1).

Table 1: Cycle of crystallization of Vita Suprinity and Celtra Duo.

	Vita Suprinity	Celtra Duo
Beginning chamber temperature (°C)	*400*	*400*
Time at the initial temperature (min)	*8*	*8*
Temperature rate increase (°C/min)	*55*	*55*
Crystallization temperature (°C)	*840*	*830*
Holding time (min)	*8*	*10*
Ending temperature (°C)	680	700

For this process, the specimens were positioned inside the oven on top of a porous refractory material allowing homogeneous heat distribution (Wendler et al., 2017). A metallic device with a central cavity and the desired dimensions (ϕ= 12 mm; 1,2 mm thick) (Figure 1) was built up to allow the better polishing of the specimens in a polishing machine (Ecomet 250 Grinder Polisher, Buehler, Illinois, USA), with silicon carbide papers of #400-,600-, 1200, and 2500 grit (Buehler Carbimet, Illinois, USA). The specimens had the final dimensions according to ISO 6872 (2008), being that 12 mm in diameter and 1.2 mm thickness. The effective polishing improves the strength of glass-ceramic following surface damage by removing a zone of deformation surrounding surface defects (Cook et al., 1981).

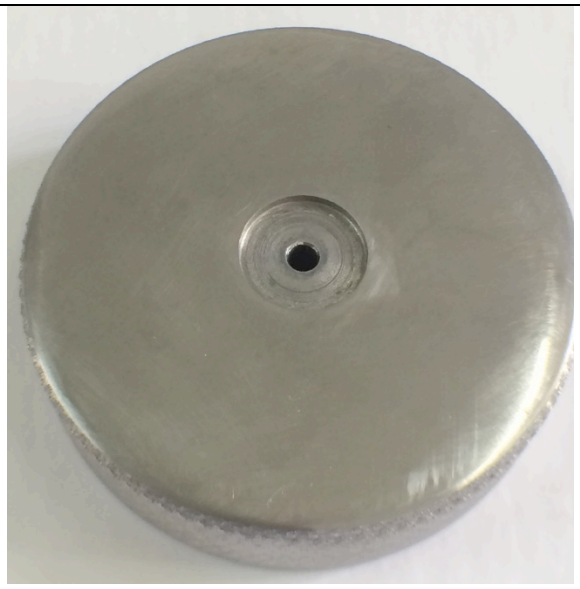


Figure 1: Stainless steel metallic device made with a central cavity with dimensions of 12 mm and 1.2 mm of thickness to aid in the polishing of the ceramic discs.

Twenty samples were randomly allocated to complementary analysis, and received a manual polishing with felt wool discs (Kota, São Paulo, Brazil) at 5,000 rpm, under refrigeration by the same abrasive liquid solution with a diamond powder in suspension (grit of 15 μm and 0.6 μm; Extec Corp, Enfield, CT, USA) for 30 s each, until the discs surfaces were shining and without scratches.

2.2 Biaxial flexural strength tests and Weibull analysis

To determine the flexural strength, the samples (n= 120) were subject to a biaxial flexural strength test according to ISO 6872:2008. Disc-shaped specimens were positioned on three support balls (3.2 mm in diameter), which were placed 10 mm equidistant each other in a triangular position. The tests were performed in water, and a flat circular piston (diameter: 1.6 mm) accomplished to a load cell of 1,000 kgF in a universal testing machine (Emic DL-1000, Emic, São José dos Pinhais, Paraná, Brazil) applied the load (1 mm/min) in the center of a superior surface of the samples until the catastrophic failure occurred. An adhesive tape (3M

ESPE, USA) was placed in the compressive side of the samples to provide better contact distribution between the piston and the ceramic discs, and to avoid spreading the fragments (Pereira et al., 2015). The biaxial flexure strength (σ) (MPa) was calculated according to ISO 6872, previously described by Ramos et al., 2016, and the strength calculations were based on the following equation:

$$\sigma = -0{,}2387P \frac{(X - Y)}{b^2}$$

Where P is the load in Kgf, X and Y are the parameters related to elastic properties of the material (Poisson's ration and Young's modulus, previously described by Wendler et al., 2017), and b is the specimen thickness in the origin of fracture in mm.

The data obtained in the flexural strength test were recorded, and submitted to Weibull analysis, using the biparametric distribution described by Quinn and Quinn (2010), in the following equations:

$$P_f = 1 - \exp -\left(\frac{\sigma}{\sigma_m}\right)^m$$

$$\ln(1 - P_f) = \left(\frac{\sigma}{\sigma_m}\right)^m$$

$$\ln\left[\ln\left(\frac{1}{1 - P_f}\right)\right] = n\ln\sigma - m\ln\sigma_\Theta$$

The statistical differences among the characteristic strength data were determined by no overlap of the 95% confidence intervals. Mean and standard deviation of flexural strength were also submitted to 2-way Anova (α=.5) and Tukey's test.

2.3 Vickers hardness and fracture strength toughness (K_{IC}) by the indentation method

Extra ceramic specimens of both ZLS materials were submitted to a mirror-polished face indented in a Vickers microhardness tester (Shimadzu Micro Hardness tester, HMV-G 21DT model, Shimadzu, Kyoto, Japan) with a load of 0.1 N for 10 s, which produces an acceptable crack pattern, following the ASTM C 1327-03 (ASTM Standard C1327) recommendations (Fig. 2A-C).

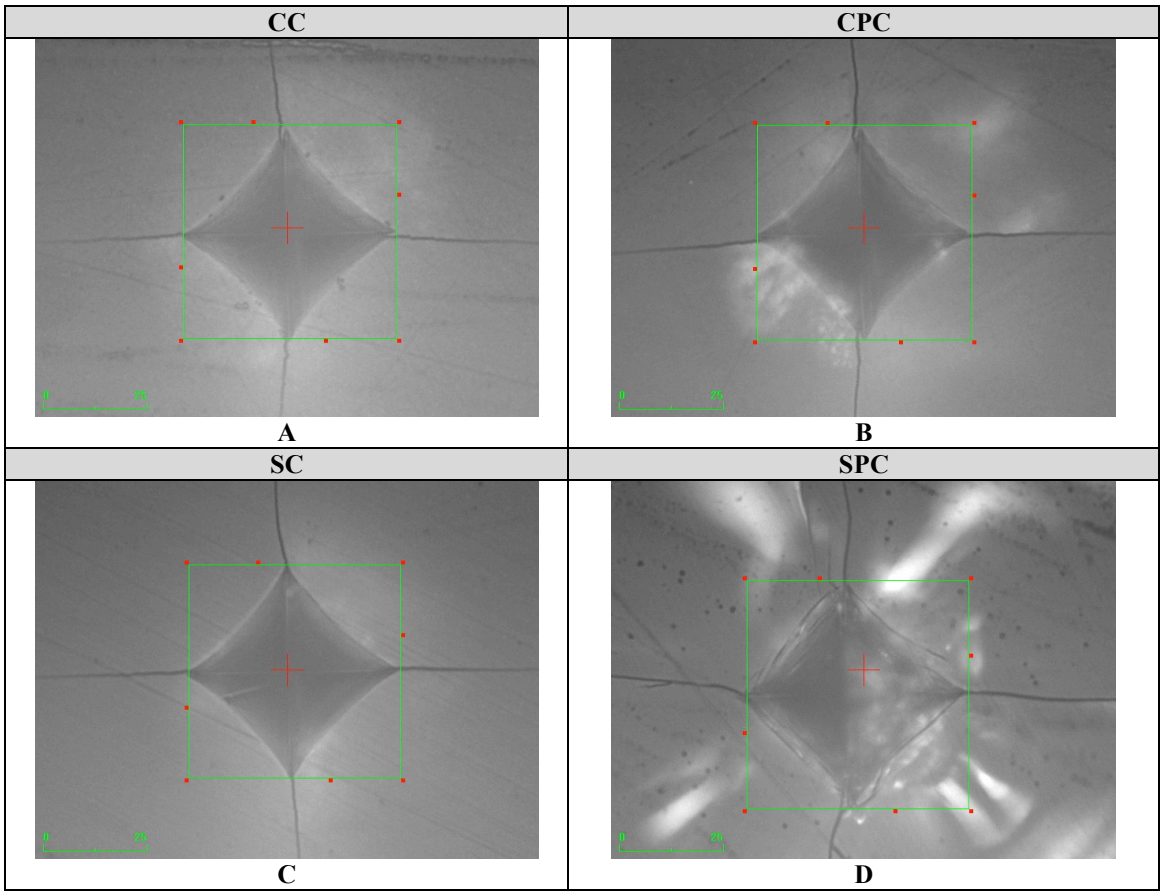


Figure 2: Vickers indentation in one representative investigated specimen for group: (A) CC, (B) CPC, (C) SPC and (D) SC.

Five indentations (10 × magnification) were made in each sample, with at least a 0.5 mm distance each other. The indentation area was automatically calculated by a software (HMV-G Series Test Software, Shimadzu Corporation, Japan), from microscopic measurements of the diagonals of impression (ASTM Designation E384-89). The Vickers hardness was obtained by the equation: $HV = 1.854\ F/d^2$, where HV is the Vickers hardness, F is the load in Kgf, and d is the arithmetical average between two diagonals in mm (indentation area). One-way ANOVA and Tukey's test ($p<.05$) were used to find the statistical differences among the groups, using the data obtained of Vickers hardness (mean and standard deviation) of each material (n= 15).

The mean length of the cracks was obtained by the indentation method (Vickers), as soon as possible, after the hardness tests, to avoid the slow crack grow after the indentation. To determinate the fracture toughness values, the ASTM Standard C1327 was used. The fracture toughness of the samples (in $MPA.m^{1/2}$) was estimated from measurement of the cracks made by indentation according to ISO 15732:2003 and JIS R 1607:2010 (Shimadzu Corporation, 2012), using the following equation: $Kc= 0.026\ E^{½}\ P^{½}\ a/C^{3/2}$, where Kc is the fracture toughness in $MPa.m^{1/2}$, E is the elastic modulus in Pa, P is the load in N, C is ½ of the mean length of the crack in μm, and a is the ½ of the mean length between the diagonal lines of indentation in m.

The values obtained (mean and standard deviation) of fracture toughness (K_{IC}) (n= 10), and the mean length of the cracks are presented in Table 2. Data were analyzed by one-way ANOVA, and Tukey's test ($p<.05$).

2.4 Field Emission - Scanning Electron Microscope – (FEG-SEM), Energy dispersive X-ray spectroscopy (EDS), and X-ray Diffraction (XRD)

The FEG-SEM analysis were performed in samples with polished surfaces that received 10% hydrofluoric acid etching (Dentsply, Brazil) for 20 s, following the manufacturer's recommendation. The specimens were examined in a Scanning Electron Microscope (MEV) with a Field Emission of high resolution (FEI) (Magellan 400L, FEI Company, Brno, Czech Republic) with a secondary electron detector (SE) and a backscattered scanning electron (BSE) allowing the size and shape of the grains could be observed under magnifications of 10000×, 40000×, and 100000×.

The chemical composition of the micro compounds was realized by Energy Dispersive X-ray spectroscopy (EDS) (Bruker Nano GmbH 410, Berlin, Germany).

An x-ray diffractometer (XDR) (X'pert Powder, PANalytical, Almelo, Netherlands) was used to identify the crystalline content in one specimen per group, by a software with a data base X'Pert HighScore (PANalytical, Netherlands).

2.5 Fractographic analysis

The deep of defect and the extent of the fractured surface was analyzed in all tested samples under a stereomicroscope (Discovery V20, Carl Zeiss, Gottingen, Germany). One representative specimen of each group was examined in SEM (Inspect S50, FEI Company, Brno, Czech Republic) at ×200 and ×1000 magnifications.

3. Results

3.1 Biaxial flexure strength tests and Weibull parameters

The ceramic materials properties measured in different stages of crystallization firing process and the Weibull parameters are described in Table 2.

Table 2: Weibull modulus (m), confidence interval of Weibull modulus (CI), characteristic strength (σ_0) of the materials, with minimum–maximum values (MPa), Vickers Hardness (GPa), fracture toughness (K_{IC}), average crack length (μm).

	SPC	SC	CPC	CC
m	7.07	5.38	5.86	5.77
CI (lower - upper)	6.24-8.00	4.01-7.23	5.10-6.74	4.29-7.76
σ_0 (MPa)	106.95	191.02	163.86	251.25
Mininum - maximum (σ_0)	100.94 - 113.33	178.10 - 204.89	153.21 - 175.26	235.36 - 268.21
Vickers Hardness (GPa)	597,533 ± 33,97 ^{B}	683,267 ± 16,07 ^{A}	682,400 ± 15,31 ^{A}	693,333 ± 10,85 ^{A}
K_{IC} (MPa.m$^{1/2}$)	2,21 ± 0,11^{a}	2,63 ± 0,14 ^{a}	2,26 ± 0,80 ^{a}	2,51 ± 0,59 ^{a}
Average crack lenght (μm)	55,77 ± 1,59	52,10 ± 0,61	52,14 ± 0,58	51,72 ± 0,40

PCC and PCS are statistically similar due to the overlap of confidence intervals on Weibull coefficient. The CS ceramic presented a lower Weibull modulus, indicating a lower structural reliability. CC presented higher characteristic strength (251.25 MPa), and its confidence interval does not overlap the other ceramic materials (CC > CS > PCC >

PCS). PCS showed a lower characteristic strength (106.95 MPa), and a higher reliability. The crystallization firing process had a directly influence on flexural strength, since the crystallized samples presented higher characteristic strength values.

3.2 Vickers hardness and fracture strength toughness (K_{Ic}) by the indentation method

CC, PCC and CS presented hardness statistically similar while PCS was statistically different, being that a lower hardness than other groups.

3.3 Microstructure characterization

The results get with the superficial damage analysis made by Vickers indentation on four structures studies are presented individually, and described in Table 2. The images of Vickers indentation on the sample's surfaces is presented on Figure 2.

By the XRD analyses (Figure 3) it is depicted that on PCS, the large picks correspond to formation of nanocrystalline lithium metasilicate. The samples CC, PCC and CS show lithium metasilicate ($Li_2SiO_{3),}$ lithium disilicate ($Li_2Si_2O_3$), tetragonal cristobalite, alfa cristobalite (ie., cristobalite correspond to formation of crystalline siliceous oxide). CC presents a small tetragonal zirconia pick, and it is not present on the material after crystallization process (PCC), showing that the crystallization firing process is necessary to crystallize zirconia. CS did not present a high and clear pick of tetragonal zirconia, indicating a lower compound of crystallized zirconia.

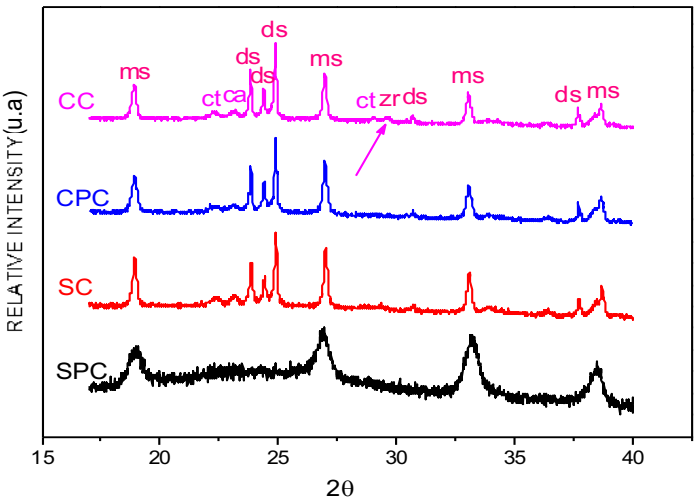


Figure 3: (XRD) SPC, SC, CPC, and CC refer respectively to: Partially Crystallized Suprinity; Crystallized Suprinity; Partially Crystallized Celtra and Crystallized Celtra. ms = lithium metasilicate, ds = lithium disilicate, ca = cristobalite alfa, ct = tetragonal cristobalite, zr = tetragonal zirconia.

Table 3 shows the chemical constituents of the studied materials after crystallization firing process. CC and CS presented similar percentile values in atomic mass, however, as expected, the lithium, one of the main compound of both ceramic materials, could not be identified by EDS. In this sense, it cannot be said that they have the same composition.

Table 3 - Composition in percentage of mass (in percentage) of the ceramics by analysis with EDS.

CERAMICS	SC	CC
Oxigen	52.60	53.09
Silicon	30.95	30.85
Zirconio	13.00	12.50
Potassium	2.06	2.36
Aluminum	1.35	1.17

The micrographs in FE-SEM corresponding to secondary electron (SE) and back scattering electron (BSE) are presented in Figure 4. In the images from CC is possible to see round grains apparently monodisperse between 1 μm and 500 nm joint by a lower quantity of glassy phase, being its structure similar to other sintered ceramics, such as alumina and even zirconia, as previously described by Belli et al. (2017). It is also possible to identify whiteness points, with a diameter of 25 nm, that can be corresponding to zirconia grains. However, on PCC, the zirconia grains have approximately 200 nm and are present most of the time in the glassy matrix. The grains of the glassy matrix are monodispersed and bigger (diameter between 1.0 and 1.5 μm) (i.e., higher percentile of glassy matrix). On micrographs corresponding to the back-scattering electron (BSE), is possible to observe more clearly the formation of circles, which corresponding to round defects or absence of glassy matrix in some points of the samples, similar to bubbles. CS presents a bimodal distribution, being some grains in size of about 500 nm and 2 μm, joint by a glassy matrix, which presents a higher quantity when compared to CC. In the same way as on CC, the white points are indicative of zirconia grains, nevertheless, in a small quantity. PCS has a continuous matrix with little grains dispersed in a glassy matrix, with cracks uniformly distributed, and the zirconia grains present the same diameter as ones of PCC (250 nm).

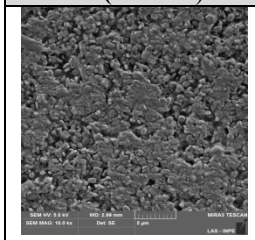
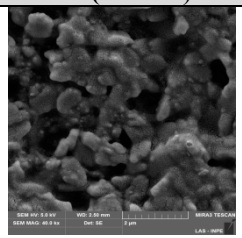
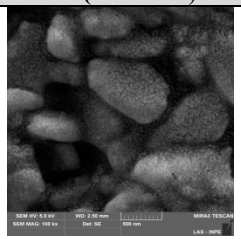
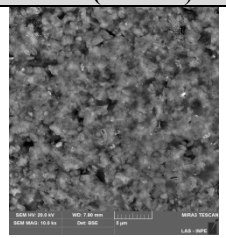
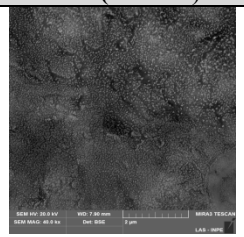
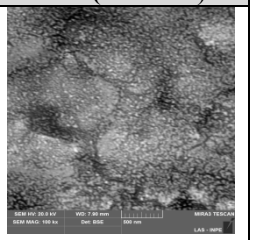
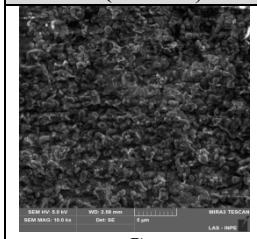
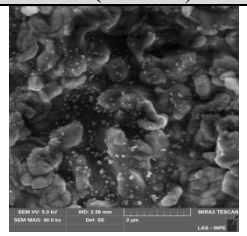
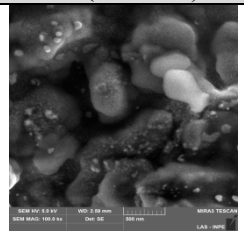
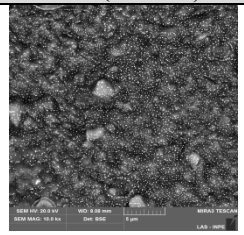
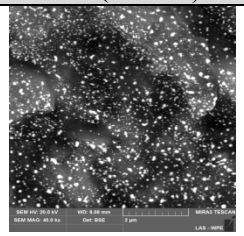
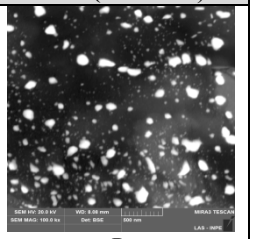
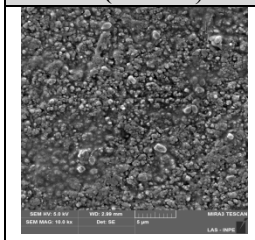
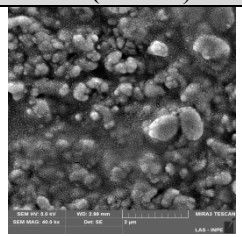
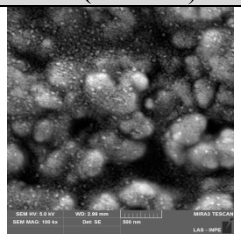
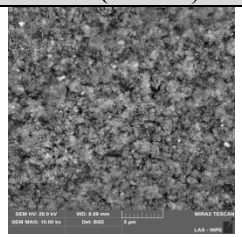
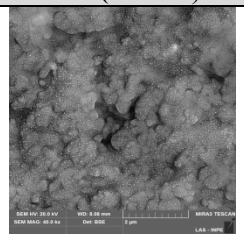
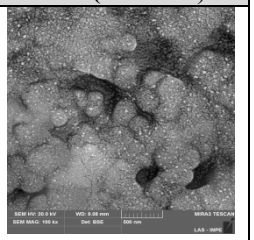
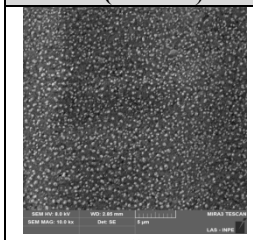
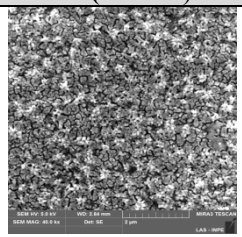
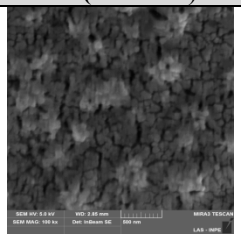
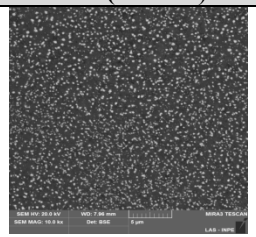
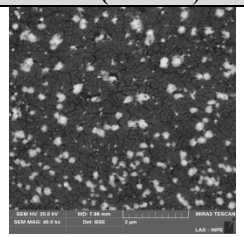
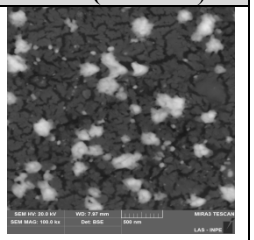
SE (10000×)	SE (40000×)	SE (100000×)	BSE (10000×)	BSE (40000×)	BSE (100000×)
					
A	**B**	**C**	**D**	**E**	**F**
SE (10000×)	**SE (40000×)**	**SE (100000×)**	**BSE (10000×)**	**BSE (40000×)**	**BSE (100000×)**
					
G	**H**	**I**	**J**	**K**	**L**
SE (10000×)	**SE (40000×)**	**SE (100000×)**	**BSE (10000×)**	**BSE (40000×)**	**BSE (100000×)**
					
M	**N**	**O**	**P**	**Q**	**R**
SE (10000×)	**SE (40000×)**	**SE (100000×)**	**BSE (10000×)**	**BSE (40000×)**	**BSE (100000×)**
					
S	**T**	**U**	**V**	**X**	**Y**

Figure 4: Representative micrographs of surface topography of the tested materials, after conditioning with 10% HF for 20 s of the CC (AF), CPC (GL), SC (MR) and SPC (SY), with SE and BSE, respectively 10000 ×, 40000 × and 100000 ×).

Figure 5 shows the SEM micrographs of the fractured surfaces of SCP, CS, PCC, and CC in different magnifications (×100 until ×1000). All the samples presented waves of energy propagation transversally directed to the principal stress, with the fracture origins in a critical defect. In the region of the critical defect is possible to observe zipper cracks (zc) in samples of CS, PCC, and CC. Debris and splinters are presented on the tensile side of PCS, compatible with high glassy phase content, and incomplete crystallization firing.

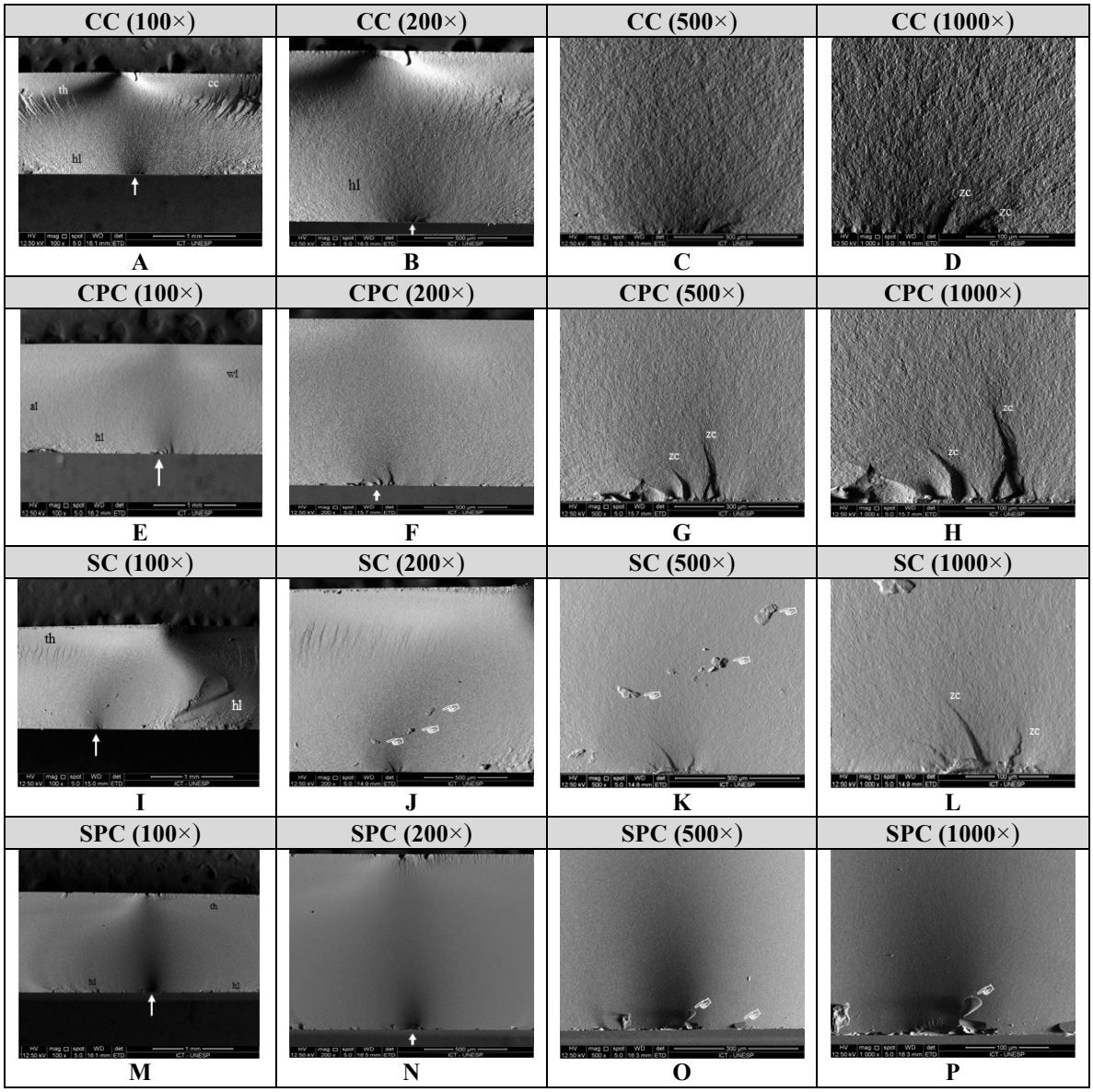


Figure 5: SEM images of fractured specimens (× 100, × 200, × 500 and × 1000 of magnification). CC (A-D); CPC (E-H); SC (I-L) and SPC (M-P). The white arrows indicate the structural flaw on the tensile surface where failure initiated. The fracture marks observed are: zc (zipper cracks), hl (hackles), th (twist hackles), cc (compression curl), al (arrest line), wl (warner lines). The zc appear as the main fracture mark in the region of the critical defect of CC, CPC and SC. The finger points indicate the presence of splinters in SC and SPC.

4. Discussion

In the present study, the null hypotheses that lithium silicate zirconia-reinforced ceramics have the same mechanical properties and microstructure before and after the fire crystallization process was denied. There is influence of the fire crystallization process on the microstructure, since it is possible to observe different tetragonal zirconia grain size, and glassy matrix quantity in both ceramics after the crystallization (Figures 3 and 4). The ceramic materials tested in their forms partially crystallized present zirconia grains with approximately 200 and 250 nm in diameter, consistent with the findings of Lawson and collaborators (2016), which state that the PCC presents a crystalline phase surrounded by a glassy matrix, with disc-shaped crystals, being probably the lithium silicate grains. Therefore, after the fire crystallization process, these crystallites appear in lower quantity, with a decreased size and more homogeneous crystal size distribution (Belli et al., 2017), and by presenting zirconia in the glassy matrix, it is believed that this ceramic material presents an additional mechanism of hardening (Ramos et al., 2016; Traini et al., 2016). In the partially crystallized forms, is also possible to see some round defects in the glassy matrix, similar to bubbles (in case of PCC) or defects for extension, such as cracks spread evenly (Figure 4).

The present study evaluated the microstructure and flexural strength of lithium silicate zirconia-reinforced glass ceramics processed by CAD/CAM technology. The crystallized forms presented similar chemical composition, based on the percentage of atomic mass of chemical elements, such as oxygenic, siliceous, zirconia (in a high mass percentage), aluminum and potassium (in a lower percentage), in agreement with the findings reported in the literature (Lawson et al., 2016). However, EDS analyses did not detect the chemical

element lithium, and due to this, it is not possible to ensure that they present the same chemical composition, different of previous studies that corroborated the lithium presence using the same method (Lawson et al., 2016; Ramos et al., 2016).

In Figure 3, X-ray diffraction results show that all ceramics present large picks of nanocrystalline lithium metasilicate (Li_2SiO_3), similar to the findings of Aurélio et al. (2017), that reported a phase stability of this material during the firing process. A previous study showed by Raman spectroscopy and X-ray diffraction that although the same crystalline and glasse phase composition were present in Suprinity and Celtra Duo, the last one presents larger Li_2SiO_3 crystallites (~1 μm) than Suprinity (~0.5 μm) (Wendler et al., 2017). The difference in size of the lithium metasilicate crystals between Suprinity and Celtra Duo may reflect in differences in crystallization firing parameters, since Celtra Duo is supplied ready-to-use while Suprinity must undergo to a shorter crystallization firing process to get ready for use. CC, PCC and CS presented lithium disilicate ($Li_2Si_2O_3$), tetragonal cristobalite, and alfa cristobalite. CC and CS did not present clearly tetragonal zirconia picks. According to Krüger et al. (2013) and Aurélio et al. (2017), the absence of crystalline zirconia after the firing process indicates that the ZrO_2 remains amorphous and aggregated to the glass matrix. The reinforcement of the glassy matrix by the dissolved zirconia particles produces a material with higher fracture toughness (Elsaka e Elnaghy, 2016; Schwindling, Rues and Schmitter, 2017). In PCC, the tetragonal zirconia also does not appear in a clear way. The crystallization firing process appear to modify the microstructure established by the manufacturer, showing that the crystallization process is necessary to change the crystalline phase.

Strength is an important mechanical property that determines the performance of brittle materials (Uctasli et al., 1996). In dentistry, the fracture

strength for a failure probability of 5% (σ= 5%) is considered more relevant clinically then for 63.2 % (σ0) (Teixeira et al., 2007; Della Bonna, Anusavice e DeHoff, 2003; Elsaka e Elnaghy, 2016). Therefore, the values of σ5% were obtained by Weibull analysis. The Weibull modulus (m) is used to illustrate the variation in strength or asymmetrical strength distribution due to flaws and microcracks which may develop within the microstructure. A lower Weibull modulus indicates more flaws and defects into the material. On the other hand, a higher Weibull modulus indicates a smaller error range and hence, greater structural reliability (Della Bonna, Anusavice e DeHoff, 2003). In the present study, the strength data were obtained by biaxial flexure strength tests, and analyzed with the Weibull parameters, to obtain the characteristic strength (σ0) and Weibull modulus (m) through the maximum probability estimation approach (EN-843-5, 1997), as well as their confidence intervals (90%) for each material and samples geometry. In this study, PCC and PCS presented overlap of confidence intervals in Weibull modulus, being that statistically similar. It is also important to highlight that CS showed Lower structural reliability because its Weibull modulus lower than others (m= 5.38). Since there was no statistical difference between the Weibull modulus for CC, PCC, and CS still supports the PCC as being the best choice to indirect ceramic restorations in dentistry. This result is in agreement with Wendler et al. (2017), who found an extremely low Weibull modulus (~ 5.5) for CS and also CC, and no statistical difference in terms of strength can be indicated between both materials, even with a tendency to lower values to CS, this material appears to be reliable for clinical use (Elsaka e Elnaghy, 2016; Schwindling, Rues and Schmitter, 2017). For CC, there was no overlap of confidence interval when compared to other ceramics, even having higher values of characteristic strength (251.25 MPa), so it is possible to allege that the fracture strength provides a security margin to use clinically this material, although the Weibull modulus observed for this material is low.

Among the tested materials, PCS presented lower values of fracture strength (σ0 = 106,95 MPa, m = 7.07), which can be explained by the limitated fracture strength toughness of this material (K_{IC} = 2,21 ± 0,11 MPa/$m^{1/2}$). These results can infer that the crystallization firing process has a directly influence on the flexural strength, since the crystallized samples presented higher characteristic strength values.

Fracture toughness is the considered the amount of energy required to a fracture some material (bulk fracture or an interface), which for linearly elastic brittle materials, the K_{IC} is the critical stress intensity factor (Quinn, 2007). Table 2 shows statistically similar values for fracture toughness of the tested materials. Among the methods used to evaluate the fracture toughness, the indentation and crack measurement method is the most common (Munz e Fett, 1999). The Vickers indentation method was used to apply a controlled damage to the studied samples (Quinn e Bradt, 2007).

The crack formation in the immediate vicinity of the pyramid indent was examined and characterized and the result is presented in the images of Figure 2. Observation of the Vicker's indents in the current study showed that CC, PCC and CS exhibited any classic Palmquist cracks, as described by Fett et al. (2005). For these materials, all radial cracks started on the lateral edge of the pyramid, near to the corner of the pyramid, with the cracks are visible along the median line of the pyramid indent (Fig. 2), which did not occur with PCS. PCS presented a cracking pattern with crack ramification, and also the collapse of the internal part of indentation, suggesting that this material present a strong indication of lower fracture toughness when compared to the other tested samples.

Fractography can help to characterize the kind of fracture mode (Harrer, Morell e Danzer, 2014). Figure 5 presents SEM micrographs of fractured samples in different magnifications (×100, ×200, ×500 and ×1000). It

is possible to note that the cracks are propagating in a perpendicular direction to the principal tensile point, in accordance with previous studies (Ramos et al., 2016; Prochnow et al., 2017), on which is stated that all the fractures started from a superficial deffect located in the tensile side of ceramic material (Quinn, 2007). In conclusion, in brittle materials such as ceramics, the appearence of fractures can occur from pre-existing defects on the surface or inside the whole structure of the ceramic material, and propagates when subject to high stress concentration, normally by a tensile stress (Prochnow et al., 2017).

It is important to elucidate some limitations of this *in vitro* study. We only evaluated the mechanical and structural properties of zirconia-reinforced lithium silicate glass ceramics. One of the limitations of the present study is that cementation procedure effect was not studied. Also, some clinical conditions were not simulated, such as the sliding that occurs during the chew, since only an axial load was applied in the center of the specimens to reproduce a monotonic load-to-failure test assembly. It is well-known that clinical stress is complex, therefore, it is difficult to determinate the condition of exact stress on which the restoration is subjected (Borba et al., 2011). In this sense, the evaluation of clinical behavior of glass-ceramics is necessary to provide reliable information to the clinicians (Rinke et al., 2015; Zimmermann et al., 2017). Another important factor to note is that the results suggest a good prognosis for the tested ceramic systems, except to the form partially-crystrallized of Suprinity. Finally, it is important to highlight that should be noted is that the polishing protocol used in the present study had only the purpose to eliminate the cut defects, and avoid pre-existing defects in the ceramic surfaces. However, this protocol does not appear to be suitable to clinical practice, since the surface polishing can increases the cement thickness and result in occlusal adjustment problems.

5. Conclusion

The conclusion drawn from our findings was as follows:
Crystallizated Celtra presented the better mechanical behavior and the higher structural homogeneity comparing to others tested materials.

References

ASTM Standard C1327. Standard test method for Vickers indentation hardness of advanced ceramics. ASTM International, West Conshohocken, PA (2015), 10.1520/C1327-15. www.astm.org

ASTM Designation E384-89. Standard test method for microhardness of materials. In: ASTM Standards. Philadelphia: American Society for Testing and Materials; 1997.

Albakry M, Guazzato M, Swain MV. Biaxial flexural strength, elastic moduli, and x-ray diffraction characterization of three pressable all-ceramic materials. J Prosthet Dent. 2003 Apr;89(4):374-80.

Aurélio IL, Dorneles LS, May LG. Extended glaze firing on ceramics for hard machining: Crack healing, residual stresses, optical and microstructural aspects. Dent Mater. 2017 Feb;33(2):226-240. doi: 10.1016/j.dental.2016.12.002.

Badawy R, El-Mowafy O, Tam LE. Fracture toughness of chairside CAD/CAM materials - Alternative loading approach for compact tension test. Dent Mater. 2016 Jul;32(7):847-52. doi: 10.1016/j.dental.2016.03.003.

Belli R, Wendler M, de Ligny D, Cicconi MR, Petschelt A, Peterlik H, et al. Chairside CAD/CAM materials. Part 1: Measurement of elastic constants and microstructural characterization. Dent Mater. 2017 Jan;33(1):84-98. doi: 10.1016/j.dental.2016.10.009.

Borba M, de Araujo MD, Fukushima KA, Yoshimura HN, Cesar PF, Griggs JA, et al. Effect of the microstructure on the lifetime of dental ceramics. Dent Mater. 2011 Jul;27(7):710-21. doi: 10.1016/j.dental.2011.04.003.

CELTRA DUO®, Celtra Block for Cerec and InLab, Dentsply Indústria e Comércio Ltda., DeguDent GmbH, Hanau, Wolfgang, Alemanha, 2014.

Cook RF, Lawn BR, Dabbs TP. Chantikul effect of machining damage on the strength of a glass-ceramic. J Am Ceram Soc. 1981, 9:C121-C122.

D'Arcangelo C, Vanini L, Rondoni GD, De Angelis F. Wear properties of dental ceramics and porcelains compared with human enamel. J Prosthet Dent. 2016 Mar;115(3):350-5. doi: 10.1016/j.prosdent.2015.09.010.

Della Bona A, Anusavice KJ, DeHoff PH. Weibull analysis and flexural strength of hot-pressed core and veneered ceramic structures. Dent Mater. 2003, 19:662-669.

Elsaka SE, Elnaghy AM. Mechanical properties of zirconia reinforced lithium silicate glass-ceramic. Dent Mater. 2016 Jul;32(7):908-14. doi: 10.1016/j.dental.2016.03.013.

EN-843-5. Mechanical testing of monolitic ceramics at room temperature. Part 5: Statistical treatment; 1997.

Fett T, Kounga N, Njiwa ABR. Crack opening displacements of Vickers indentation cracks. Engineering Fracture Mechanics. 2005, 72(5):647-659.

Harrer W, Morell R, Danzer R. Fractography of biaxial tested Si_3N_4-specimens. J Eur Ceram Soc. 2014, 34:3283-3289.

International Organization for Standardization. ISO-15732:2003. Fine ceramics (advanced ceramics, advanced technical ceramics) - Test method for fracture toughness of monolithic ceramics at room temperature by single edge precracked beam (SEPB) method. International Organization for Standardization, Geneva, 2003.

International Organization for Standardization. ISO-6872:2008. Dentistry ceramic materials. International Organization for Standardization, Geneva; 2008 (Available at http://www.iso.org/iso/store.htm).

JIS R 1607. Japanese Standards Association. Testing Methods For Fracture Toughness Of Fine Ceramics At Room Temperature. 2010.

Krüger S, Deubener J, Ritzberger C, Höland W. Nucleation kinetics of lithium metasilicate in ZrO_2-bearing lithium disilicate glasses for dental application. Int J Appl Glass Sci. 2013,4: 9-19.

Lawson NC, Bansal R, Burgess JO. Wear, strength, modulus and hardness of CAD/CAM restorative materials. Dent Mater. 2016 Nov;32(11):e275-e283. doi: 10.1016/j.dental.2016.08.222.

Lohbauer U, Scherrer SS, Della Bona A, Tholey M, van Noort R, Vichi A, Kelly JR, Cesar PF. ADM guidance-Ceramics: all-ceramic multilayer interfaces in dentistry. Dent Mater. 2017 Jun;33(6):585-598. doi: 10.1016/j.dental.2017.03.005.

Mainjot AK, Dupont NM, Oudkerk JC, Dewael TY, Sadoun MJ. From artisanal to CAD-CAM blocks: State of the art of indirect composites. J Dent Res. 2016 May;95(5):487-95. doi: 10.1177/0022034516634286.

Monteiro JB, Oliani MG, Guilardi LF, Prochnow C, Pereira GKR, Bottino MA, Melo RM, Valandro LF. Fatigue failure load of zirconia-reinforced lithium silicate glass ceramic cemented to a dentin analogue: Effect of etching time and hydrofluoric acid concentration. J Mech Behav Biomed Mater. 2008, 77:375-382. doi:10.1016/j.jmbbm.2017.09.028

Munz D, Fett T. Ceramics – Mechanical properties, failure behavior, materials selection, Springer, 1999, London.

Pereira G, Amaral M, Cesar PF, Bottino MC, Kleverlaan CJ, Valandro LF. Effect of low-temperature aging on the mechanical behavior of ground Y-TZP. J Mech Behav Biomed Mater. 2015 May;45:183-92. doi: 10.1016/j.jmbbm.2014.12.009.

Prochnow C, Venturini AB, Grasel R, Bottino MC, Valandro LF. Effect of etching with distinct hydrofluoric acid concentrations on the flexural strength of a lithium disilicate-based glass ceramic. J Biomed Mater Res B Appl Biomater. 2017 May;105(4):885-891. doi: 10.1002/jbm.b.33619.

Quinn GD. Recommended Practice Guide: Fractography of Ceramics and Glasses. Washington: National Institute of Standards and Technology (NIST), United States NIST; 2007.

Quinn GD, Bradt RC. On the Vickers indentation fracture toughness test. J Am Ceram Soc. 2007, 90(3):673-680. doi: 10.1111/j.1551-2916.2006.01482.x.

Quinn JB, Quinn GD. A practical and systematic review of Weibull statistics for reporting strengths of dental materials. Dent Mater. 2010 Feb;26(2):135-47. doi: 10.1016/j.dental.2009.09.006.

Ramos NC, Campos TM, Paz IS, Machado JP, Bottino MA, Cesar PF, et al. Microstructure characterization and SCG of newly engineered dental ceramics. Dent Mater. 2016 Jul;32(7):870-8.

Rinke S, Rödiger M, Ziebolz D, Schmidt AK. Fabrication of zirconia-reinforced lithium silicate ceramic restorations using a complete digital workflow. Case Rep Dent. 2015. doi: 10.1155/2015/162178.

Sato TP, Anami LC, Melo RM, Valandro LF, Bottino MA. Effects of surface treatments on the bond strength between resin cement and a new zirconia-reinforced lithium silicate ceramic. Oper Dent. 2016 May-Jun;41(3):284-92. doi: 10.2341/14-357-L.

Schwindling FS, Rues S, Schmitter M. Fracture resistance of glazed, full-contour ZLS incisor crowns. J Prosthodont Res. 2017, 61(3):344-349. doi: 10.1016/j.jpor.2016.12.008.

Shimadzu Micro Hardness Tester HMV-G21. Instruction Manual. Shimadzu Corporation, Japan. 2012.

Teixeira E, Piascik JR, Stoner BR, Thompson JY. Dynamic fatigue and strength characterization of three ceramic materials. J Mater Sci Mater Med. 2007, 18(6):1219-1224.

Traini T, Sinjari B, Pascetta R, Serafini N, Perfetti G, Trisi P, et al. The zirconia-reinforced lithium silicate ceramic: lights and shadows of a new material. Dent Mater J. 2016 Oct 1;35(5):748-755.

Uctasli S, Wilson HJ, Unterbrink G, Zaimoglu A. The strength of a heat-pressed all-ceramic restorative material. J Oral Rehabil, 1996, 23: 257-261.

VITA SUPRINITY®, Technical and scientific documentation, Vita Zahnfabrik, Bad Säckingen, Germany, 2014.

Wendler M, Belli R, Petschelt A, Mevec D, Harrer W, Lube T, et al. Chairside CAD/CAM materials. Part 2: Flexural strength testing. Dent Mater. 2017 Jan;33(1):99-109. doi: 10.1016/j.dental.2016.10.008.

Zimmermann M, Koller C, Mehl A, Reinhard H. Indirect zirconia-reinforced lithium silicate ceramic CAD/CAM restorations: Preliminary clinical results after 12 months. Quintessence Int. 2017;48(1):19-25.

3 CONSIDERAÇÕES GERAIS

Neste estudo atual, a hipótese nula de que as cerâmicas de silicato de lítio reforçado por zircônia possuem as mesmas propriedades mecânicas e microestruturais antes e após o tratamento térmico foi rejeitada. Há influência do tratamento térmico na microestrutura, uma vez que é possível observar diferentes tamanhos da zircônia tetragonal e quantidade de fase vítrea nas duas cerâmicas após a cristalização. As cerâmicas nas suas formas parcialmente cristalizadas apresentam grãos de zircônia com aproximadamente 200 e 250 nm de diâmetro, condizente com os achados da literatura que afirmaram que o CPC apresenta uma fase cristalina cercada por uma matriz vítrea, com cristais em forma de disco, que provavelmente são grãos de silicato de lítio. Portanto, após o tratamento térmico, esses cristais aparecem em menor quantidade, com tamanho reduzido e com a distribuição mais homogênea dos cristais e por apresentar zircônia na matriz vítrea, acredita-se que esse material tem um mecanismo de endurecimento adicional. Nas formas parcialmente cristalizadas também é possível observar alguns defeitos circulares na fase vítrea, semelhantes as bolhas (no caso da CPC) ou defeitos por extensão, como trincas espalhadas uniformemente (no caso da SPC).

Este artigo avaliou a microestrutura e a resistência à flexão de cerâmicas de silicato de lítio reforçado por zircônia processados pela tecnologia CAD-CAM. As formas cristalizadas apresentaram composição química equivalente, com base na porcentagem de massa atômica de elementos químicos como oxigênio, silício, zircônio (em maior porcentual de massa) e alumínio e potássio (em menor percentual), de acordo com os achados relatados na literatura.

Os dados de resistência obtidos nesse estudo usando o teste de flexão biaxial foram analisados usando as estatísticas de Weibull para obter a

resistência característica (σ0) e o módulo de Weibull (m) através do procedimento de estimação de máxima probabilidade, bem como seus intervalos de confiança (90%) para cada material e geometria da amostra. Nesse estudo, CPC e a SPC apresentaram sobreposição de intervalo de confiança no coeficiente de Weibull e por isso são estatisticamente semelhantes. Também destacamos que a SC detona menor confiabilidade estrutural por apresentar o menor módulo de Weibull (m = 5.38). O fato de que não houve diferença significativa entre os valores de m para os grupos CC, CPC e SC ainda apoia o uso de CPC como material de escolha para restaurações cerâmicas indiretas na prática odontológica. Na CC não há sobreposição do seu intervalo de confiança aos das outras cerâmicas, além de apresentar valores superiores de resistência característica (251,25 MPa), então, podemos afirmar que a resistência à fratura proporciona uma margem de segurança que suporta o uso clínico deste material, mesmo que sejam observados valores baixos de m. On the other side, SPC apresentou a menor força de fratura inerte entre os materiais testados (σ0 = 106,95 MPa, m = 7.07).

REFERÊNCIAS*

Albakry M, Guazzato M, Swain MV. Biaxial flexural strength, elastic moduli, and x-ray diffraction characterization of three pressable all-ceramic materials. J Prosthet Dent. 2003 Apr;89(4):374-80.

Aurélio IL, Dorneles LS, May LG. Extended glaze firing on ceramics for hard machining: Crack healing, residual stresses, optical and microstructural aspects. Dent Mater. 2017 Feb;33(2):226-40. doi: 10.1016/j.dental.2016.12.002.

Belli R, Wendler M, de Ligny D, Cicconi MR, Petschelt A, Peterlik H, et al. Chairside CAD/CAM materials. Part 1: Measurement of elastic constants and microstructural characterization. Dent Mater. 2017 Jan;33(1):84-98. doi: 10.1016/j.dental.2016.10.009.

Borba M, de Araujo MD, Fukushima KA, Yoshimura HN, Cesar PF, Griggs JA, et al. Effect of the microstructure on the lifetime of dental ceramics. Dent Mater. 2011 Jul;27(7):710-21. doi: 10.1016/j.dental.2011.04.003.

CELTRA DUO®, Celtra Block for Cerec and InLab, Dentsply Indústria e Comércio Ltda. Hanau, Wolfgang (Alemanha): DeguDent GmbH; 2014.

Chavali R, Nejat AH, Lawson NC. Machinability of CAD-CAM materials. J Prosthet Dent. 2016 Dec 23. pii: S0022-3913(16)30512-1. doi: 10.1016/j.prosdent.2016.09.022. PubMed PMID: 28024821.

Cunha LF, Gonzaga CC, Pissaia JF, Correr GM. Lithium silicate endocrown fabricated with a CAD-CAM system: a functional and esthetic protocol. J Prosthet Dent. 2017. doi: 10.1016/j.prosdent.2016.10.006.

Della Bona A. Adesão às cerâmicas: evidências científicas para o uso clínico. São Paulo: Artes Médicas; 2009.

Elsaka SE, Elnaghy AM. Mechanical properties of zirconia reinforced lithium silicate glass-ceramic. Dent Mater. 2016 Jul;32(7):908-14. doi: 10.1016/j.dental.2016.03.013.

---

* Baseado em: International Committee of Medical Journal Editors Uniform Requirements for Manuscripts Submitted to Biomedical journals: Sample References [Internet]. Bethesda: US NLM; c2003 [atualizado 04 nov 2015; acesso em 25 jan 2017]. U.S. National Library of Medicine; [about 6 p.]. Disponível em: http://www.nlm.nih.gov/bsd/uniform_requirements.html

Gracis S, Thompson VP, Ferencz JL, Nelson RFA, Bonfante A. A New classification system for all-ceramic and ceramic-like restorative materials. Int J Prosthod. 2015; 28(3):227-35.

Guess PC, Zavanelli RA, Silva NR, Bonfante EA, Coelho PG, Thompson VP. Monolithic CAD/CAM lithium disilicate versus veneered Y-TZP crowns: comparison of failure modes and reliability after fatigue. Int J Prosthodont. 2010 Sep-Oct;23(5):434-42.

Kassardjian V, Varma S, Andiappan M, Creugers NHJ, Bartlett S. A systematic review and meta analysis of the longevity of anterior and posterior all-ceramic crowns. J Dent. 2016 Dec;55-1-6. doi: 10.1016/j.jdent.2016.08.009.

Lien W, Roberts HW, Platt JA, Vandewalle KS, Hill TJ, Chu T-MG. Microstructural evolution and physical behavior of a lithium disilicate glass-ceramic. Dent Mater. 2015;31(8):928-40. doi: 10.1016/j.dental.2015.05.003.

Lohbauer U, Frankenberger R, Krämer N. Surface quality controls mechanical strength and fatigue lifetime of dental ceramics and resin composites. Ceram Mater. 2010;9:176-97.

Mark JE. Ceramic-reinforced polymers and polymer-modified ceramics. Polym Eng Sci. 1996 Dec;36(24):2905-20.

Mainjot AK, Dupont NM, Oudkerk JC, Dewael TY, Sadoun MJ. From artisanal to CAD-CAM blocks: State of the art of indirect composites. J Dent Res. 2016 May;95(5):487-95. doi: 10.1177/0022034516634286.

Martins LM, Lorenzoni FC, Farias BC, Lopes LDS, Bonfante G, Rubo JH. Comportamento biomecânico das cerâmicas odontológicas: revisão. Cerâmicas. 2010;56:148-55.

Petrini M, Ferrante M, Su B. Fabrication and characterization of biomimetic ceramic/polymer composite materials for dental restoration. Dent Mater. 2013 Apr;29(4):375-81. doi: 10.1016/j.dental.2012.12.004.

---

* Baseado em: International Committee of Medical Journal Editors Uniform Requirements for Manuscripts Submitted to Biomedical journals: Sample References [Internet]. Bethesda: US NLM; c2003 [atualizado 04 nov 2015; acesso em 25 jan 2017]. U.S. National Library of Medicine; [about 6 p.]. Disponível em: http://www.nlm.nih.gov/bsd/uniform_requirements.html

Quinn GD. Fractography of ceramics of ceramics and glasses. Washington: NIST; 2007.

Ramos NC, Campos TM, Paz IS, Machado JP, Bottino MA, Cesar PF, et al. Microstructure characterization and SCG of newly engineered dental ceramics. Dent Mater. 2016 Jul;32(7):870-8.

Rinke S, Rödiger M, Ziebolz D, Schmidt AK. Fabrication of zirconia-reinforced lithium silicate ceramic restorations using a complete digital workflow. Case Rep Dent. 2015. doi: 10.1155/2015/162178. PubMed PMID: 26509088.

Sato TP, Anami LC, Melo RM, Valandro LF, Bottino MA. Effects of surface treatments on the bond strength between resin cement and a new zirconia-reinforced lithium silicate ceramic. Oper Dent. 2016 May-Jun;41(3):284-92. doi: 10.2341/14-357-L.

Schwindling FS, Rues S, Schmitter M. Fracture resistance of glazed, full-contour ZLS incisor crowns. J Prosthodont Res. 2017 Jan 19. pii:S1883-1958(16)30114-1. doi: 10.1016/j.jpor.2016.12.008. PubMed PMID: 28111135.

Shimadzu Micro Hardness Tester HMV-G21. Instruction Manual. Quioto (Japan): Shimadzu Corporation; 2012.

Silva NR, Bonfante EA, Martins LM, Valverde GB, Thompson VP, Ferencz JL, et al. Reliability of reduced-thickness and thinly veneered lithium disilicate crowns. J Dent Res. 2012 Mar;91(3):305-10. doi: 10.1177/0022034511433504.

Traini T, Sinjari B, Pascetta R, Serafini N, Perfetti G, Trisi P, et al. The zirconia-reinforced lithium silicate ceramic: lights and shadows of a new material. Dent Mater J. 2016 Oct 1;35(5):748-55.

VITA SUPRINITY®, Technical and scientific documentation, Vita Zahnfabrik, Bad Säckingen, Germany, 2014.

Wendler M, Belli R, Petschelt A, Mevec D, Harrer W, Lube T, et al. Chairside CAD/CAM materials. Part 2: flexural strength testing. Dent Mater.
2017 Jan;33(1):99-109. doi: 10.1016/j.dental.2016.10.008. PubMed PMID: 27884403.

---

* Baseado em: International Committee of Medical Journal Editors Uniform Requirements for Manuscripts Submitted to Biomedical journals: Sample References [Internet]. Bethesda: US NLM; c2003 [atualizado 04 nov 2015; acesso em 25 jan 2017]. U.S. National Library of Medicine; [about 6 p.]. Disponível em: http://www.nlm.nih.gov/bsd/uniform_requirements.html

Zarone F, Ferrari M, Mangano FG, Leone R, Sorrentino R. Digitally oriented materials: focus on lithium disilicate ceramics. Int J Dent. 2016. doi:10.1155/2016/9840594. PubMed PMID: 9840594.

Zimmermann M, Koller C, Mehl A, Reinhard H. Indirect zirconia-reinforced lithium silicate ceramic CAD/CAM restorations: preliminary clinical results after 12 months. Quintessence Int. 2017;48(1):19-25

* Baseado em: International Committee of Medical Journal Editors Uniform Requirements for Manuscripts Submitted to Biomedical journals: Sample References [Internet]. Bethesda: US NLM; c2003 [atualizado 04 nov 2015; acesso em 25 jan 2017]. U.S. National Library of Medicine; [about 6 p.]. Disponível em: http://www.nlm.nih.gov/bsd/uniform_requirements.html