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**University of Minho**



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**DOCTORAL PROGRAM IN MECHANICAL ENGINEERING**

**DOCTORAL THESIS**

*Study of porcelain-zirconia composites for dental applications*

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DE MATERIAIS

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## ***Dedication***

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*This thesis is dedicated to my parents...*



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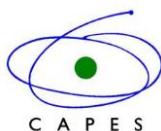
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## **Abstract**

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### *Study of porcelain-zirconia composites for dental applications*

All-ceramic restorations have been widely used as aesthetic standard in nowadays dentistry, to replace the tooth structure (appearance and function). However, failures associated with chipping and delamination of the veneering porcelain from zirconia substructure still high when compared to metal-ceramic systems. This study aimed address these problems by improving the mechanical strength of veneering porcelain and by improving its adhesion to zirconia substrate. First, the addition of a stronger ceramic second phase (zirconia particles) to feldspathic porcelain was studied. This study began with the preliminary characterization of zirconia synthesized by Complex Polymerization Method (CPM) and commercial zirconia. It was found that the synthesized zirconia did not show improved properties when compared to commercial zirconia. Commercial zirconia powders were thus used thereafter. The influence of the type of powder (pre-sintered or agglomerated) in the mechanical properties and wear of porcelain composites (20vol.%) was evaluated. The pre-sintered powders increased the mechanical strength and wear of the composites compared to agglomerated powders. Then, it was determined the amount of second phase (0-50vol.%) that maximizes the mechanical properties of the porcelain-zirconia composites. It was concluded that the composites with 30vol.% of zirconia showed the best results for wear and flexural strength (198.5MPa). Finally, it was evaluated the influence of the type of surface treatment (sandblasting or holes) and the deposition of a composite interlayer (porcelain reinforced with 30vol.% of zirconia), on the zirconia surface, on the bond strength between the veneering porcelain and the zirconia substructure. The highest bond strength values were found for specimens having simultaneously holes on the surface of zirconia and the composite interlayer between the zirconia substructure and the veneering porcelain ( $138 \pm 19$ MPa). It was demonstrated that the correct configuration of the interface between the zirconia substructure and the veneering porcelain can lead to all-ceramic restorations with enhanced mechanical strength and improved clinical performance.

**Keywords:** Feldspathic porcelain, Zirconia, CPM, Hot pressing, Mechanical Properties, Composites.

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## **Resumo**

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### *Estudo dos compósitos de porcelana-zircônia para aplicações odontológicas*

Restaurações totalmente cerâmicas tem sido largamente empregada como padrão em odontologia, na substituição da estrutura dentária (aparência e função). Contudo, as falhas por lascamento e delaminação da porcelana e da subestrutura de zircônia continuam se apresentando elevadas face às verificadas em sistemas metalo-cerâmicos. Assim, este estudo visou melhorar quer a resistência mecânica da porcelana de revestimento quer a sua adesão ao substrato de zircônia em sistemas cerâmicos utilizados em restaurações dentárias. Primeiramente estudou-se a inserção de uma segunda fase cerâmica mais resistente (zircônia) na porcelana feldspática de revestimento. Esta fase iniciou com uma prévia caracterização da zircônia sintetizada via Método de Complexação Polimérica (CPM) e zircônia comercial. Concluiu-se que a zircônia sintetizada não apresentava propriedades melhoradas face à zircônia comercial, sendo utilizada a zircônia comercial nos estudos subsequentes. A influência do tipo de pó (aglomerado ou pré-sinterizado) nas propriedades mecânicas e de desgaste dos compósitos de porcelana (20vol.%) foi avaliada. Os pós pré-sinterizados aumentaram a resistência mecânica e de desgaste do compósito em comparação aos pós aglomerados. Posteriormente, realizou-se a determinação da quantidade de segunda fase (0-50vol.%) que maximizasse as propriedades mecânicas dos compósitos porcelana-zircônia. Concluiu-se que os compósitos com (30vol.%) de zircônia apresentaram os melhores resultados de desgaste e resistência a flexão (198,5MPa). Finalmente, foi avaliada a influência do tratamento superficial da subestrutura de zircônia (jateamento e furos) e a inserção de uma camada intermediária compósita (porcelana reforçada com 30vol.% de zircônia) na resistência de adesão porcelana/subestrutura. Os maiores valores de adesão foram registrados quando da utilização simultânea de furos e da camada intermediária compósita ( $138\pm19$ MPa). Com isso, verifica-se que a correta configuração da interface zircônia-porcelana pode produzir restaurações cerâmicas com propriedades acrescidas de resistência mecânica, as quais devem melhorar significativamente o seu desempenho clínico.

**Palavras-chave:** Porcelana feldspática, Zircônia, CPM, Prensagem à quente, Propriedades Mecânicas, Compósitos.

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## ***List of Abbreviations***

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CPM – Complex Polymerization Method

XRD – X –Ray diffraction

Y-TZP – Yttria – Tetragonal Zirconia Polycrystals

TGA/DTA – Thermogravimetric analysis

SEM – Scanning Electron Microscopy

FEG-SEM – Field Emission Guns Electron Microscopy

EDS – Energy Dispersion Spectroscopy

KIC – Fracture Toughness

HV – Hardness

E – Young's Modulus

PMMA – polymethylmethacrylate

CTE – Coefficient of Thermal Expansion

COF – Coefficient friction

CNC – Milling Machine

CAD – Computer Aided Design

Ra – surface roughness

UFRN – Federal University of Rio Grande do Norte

UMINHO – University of MINHO

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## ***Scope and structure of the thesis***

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This thesis is elaborated in 8 chapters. ***Chapter 1*** gave a general introduction including a literature overview on the aspects related to the dental applications specifically to ceramic-ceramic materials. The topics dealt with are: 1.1 Teeth (Function and Structure), 1.2 Dental materials, 1.3 Dental ceramics, 1.3.1 Dental porcelain classification, 1.3.2 Porcelain Composition, 1.3.3 Processing, 1.3.4 Sintering Cycles, 1.4 All ceramic restorations, 1.4.1 Zirconia, 1.4.2 Synthesis of Zirconia, 1.5 Particulate Composites, 1.6 Ceramic-Ceramic composites interaction/Adhesion, 1.6.1 Bond Strength Tests and 1.7 Applications of dental Ceramic.

The following chapters contain 6 research reports that receive Introduction, Experimental Procedure (Materials and Methods), Results, Discussion and Conclusions of the experimental work, performed during this study.

In ***Chapter 2***, details about the previous characterization and comparative study of commercial zirconia (Y-TZP) and zirconia powders obtained by CPM (Complex Polymerization Method). This comparison is based in a different technique of manufacture applied and the use of Yttria content (3, 4 and 5 mol.%) in zirconia synthesized as also theirs implications arising during the processing. This paper is submitted for publication in Quimica Nova.

***Chapter 3***, is devoted to the study of the mechanical behavior of different types of zirconia powders incorporated on feldspathic porcelain matrix. The first tests were performed using two types of particles (yttria-stabilized zirconia ( $ZrO_2\text{-}3\%Y_2O_3$ ) agglomerates and pre-sintered yttria-stabilized zirconia ( $ZrO_2\text{-}3\%Y_2O_3$ )) in a 20% vol.% of proportion. These results were compared to feldspathic porcelain on strengthening and toughening behavior. This paper is published in International of Medical, Health, Biomedical and Pharmaceutical Engineering (Vol. 9 No.5 2015).

***Chapter 4***, is based in Chapter 3 from the superior mechanical properties of the zirconia particles in porcelain matrix. Thus, the reinforcements are incorporated in feldspathic porcelain matrix in different volume contents (0-50% vol.%) and are evaluated the microstructural characteristics by Scanning Electron Microscopy (SEM), Energy Dispersion Spectroscopy (EDS) and XRD Diffraction (XRD) and mechanical performance by the transverse rupture strength test. This paper is submitted to the journal Dental Materials - Elsevier.

**Chapter 5**, examines the wear behavior of dental composites reinforced by 20% vol.% (tetragonal zirconia 3Y-TZP). The results are compared between two types of particles (agglomerates and pre-sintered particles) and monolithic porcelain. This paper is submitted for publication in Journal of Dentistry.

**Chapter 6**, the wear characterization of dental feldspathic porcelain reinforced by Yttria-Stabilized Zirconia in different volume contents (0-50% vol.%) are performed. The results are compared as monolithic porcelain in wear resistance, coefficient of friction and hardness. This paper is submitted to the journal Dental Materials.

**Chapter 7** is devoted to the experimental evaluation of the bond strength between zirconia substructure and porcelain through a composite ceramic-ceramic graded transition interlayer. Several ceramic-ceramic were produced and tested as interlayers aiming at the improvement of ceramic-ceramic adhesion. The bond strength results are compared as substructures with/without interlayer and different surface treatments. This paper is submitted to the journal Dental Materials.

Finally, **Chapter 8** addresses a general discussion and the main conclusions are drawn. In this chapter also presented a perspective for future works.

In this thesis, all chapters can be read independently because they have been written in a form which suited for publication in international scientific journals, according to the rules of the University of Minho and UFRN.

## ***Motivation and aim of this thesis***

---

The tooth structure and teeth loss cause problems related to the health (teeth function) and discomfort in social environment. The development of the materials and processing methods in terms of mechanical properties, wear resistance, chemical attack resistance have gained the researcher's attention in the last four decades, by improving of the suitable replacement of the natural teeth. Such characteristics cannot be reached only to monolithic materials or layers processing, whereas the real tooth structure it is more complex. Based on the previously stated, various materials and composites have been used to minimize these undesirable effects, e.g., metal-ceramic restorations, related to reestablish function and aesthetics. However, these materials required considerable reduction of the tooth structure.

In this context, ceramic materials, e.g., zirconia-based materials has been widely used in dental studies due to good mechanical properties in addition to aesthetics appearance. In another hand, the success of all-ceramic restorations depends of a strong bond between ceramic feldspathic and zirconia substructure. These materials had to be adapted, e.g., in the thermal expansion coefficient and firing temperature to achieve optimal bonding.

The idea of this thesis is based on previous studies (Huang et al 2014, Henriques et al 2012; Zhang et al, 2004) which uses different contents of reinforcement (metals and ceramics) in porcelain matrix. Based on these ideas, the studies were outlined in evaluate of the mechanical performance, wear, substructure surface and interaction veneer-core, and core itself may contribute to the performance of the restorations. Thus, the influence of processing, type of powders and zirconia volume content in porcelain matrix was assessed.

The above factors emphasize, the aim of this thesis for further investigations on porcelain-zirconia composites, the improvement of all-ceramic restorations, and especially the interaction of zirconia used as reinforcement and porcelain (veneering) and its influence on the performance of the whole restoration. Thus, the general and specific objectives can be drawn:

## ***General Objective***

The aim of this study was to evaluate the mechanical properties and microstructural characteristics of a dental ceramic feldspathic reinforced zirconia in different aspects (Obtaining method, type and volume content of reinforcement) on mechanical, wear and adhesion/interaction (bond strength) behavior.

## ***Specific Objectives***

- Comparative study between commercial zirconia and zirconia synthesized with Yttria content and calcination temperatures by Complex Polymerization Method (CPM). (*Chapeter 2*);
- Strengthening and toughening of dental porcelain by the inclusion of the different types of yttria-stabilized zirconia as reinforcing phase (*Chapter 3*);
- Mechanical and microstructural study of zirconia in varied volume contents reinforced dental porcelain composites (*Chapter 4*);
- Wear performance of dental porcelain composites reinforced by different types of yttria-stabilized zirconia (*Chapter 5*).
- Tribological behavior of dental porcelain composites reinforced by different volume contents (0-50%) of yttria-stabilized zirconia (*Chapter 6*).
- Effect of CNC-created surface holes and of a composite interlayer on the shear bond strength of porcelain to zirconia substructures (*Chapter 7*).

# **CHAPTER I**

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## **1. Introduction**

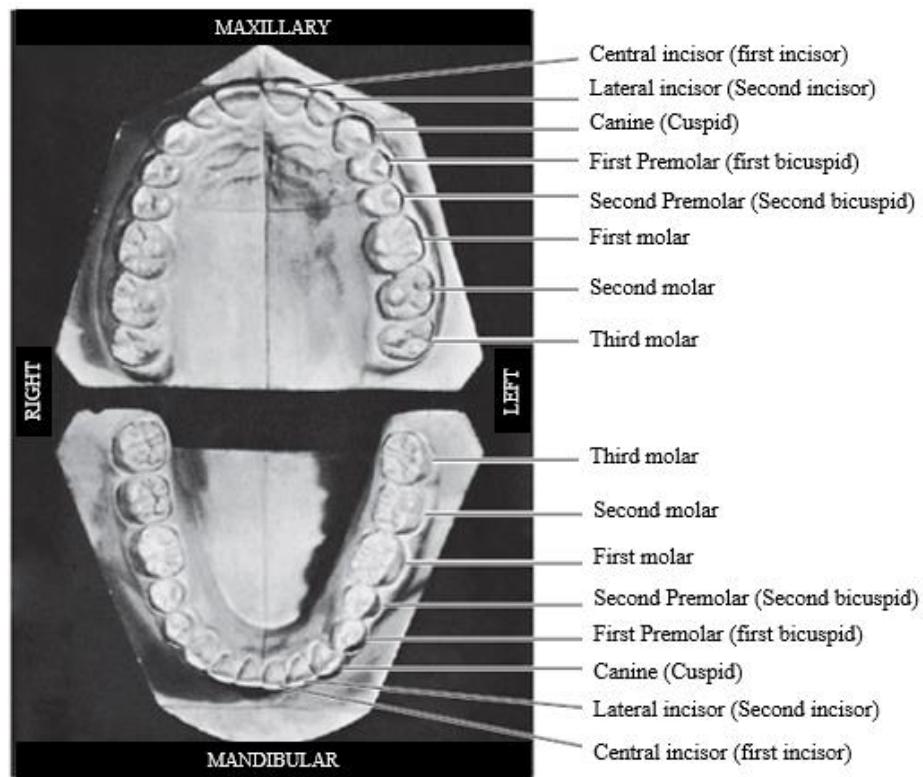
The technological evolution of dental ceramics, have been remarkable over the past four decades to replace the natural tooth. From feldspathic porcelains to zirconia-based all-ceramics, tremendous progress have been made in terms of mechanical performance. In this context, this chapter present a literature overview on the aspects related to the dental applications and specifically in ceramic-ceramic systems.

### **1.1 Teeth (Function and Structure)**

Tooth is a hard structure, protruding whitish composed of pulp, dentin and enamel which is implanted in the jaw and mandible (or dental records in human) of many vertebrates (Stuart, 2004). It is used to cut, hold and grind food, starting the digestion process from the swallowing. Teeth are also importance in helping correct sound pronunciation, speech articulation and facial expression.

The first step in understanding dental anatomy is to learn the nomenclature used to describe or classify the material included in the subject. The dental anatomy may be divided in two terms: mandibular (lower jaw or mandible) and maxillary (upper jaw or maxila). When, more than one name is used in literature to describe something, the two most commonly used names will be used initially. After that, they may be combined or used separately as consistent with the literature of a particular specialty of dentistry, for example, primary or deciduous dentition, permanent or succedaneous dentition (Nelson & Ash, 2010).

In a human adult, the permanent dentition consisting of 32 teeth is completed from 18 to 25 years of age if the third molar included and can be divided: 16 in the upper maxillary arch and 16 in the lower mandibular arch (Fig 1.1). The teeth can be classified in incisors, canines, premolars, molars and wisdom teeth or third molar.



**Fig 1.1.** A, Casts of deciduous, or primary, dentition. B, Casts of permanent dentition.

(Adapted Berkovitz et al, 2002).

**Incisors (8 total):** The middlemost four on the upper and lower jaws. Incisor teeth are the teeth at the front of the mouth, and they are adapted for plucking, cutting, tearing, and holding. The biting portion of an incisor is wide and thin, making a chisel-shaped cutting edge. The upper incisors have a delicate tactile sense that enables them to be used for identifying objects in the mouth by nibbling.

**Canines (4 total):** Next to incisors on each side is a canine, or cuspid tooth. It frequently is pointed and similar to incisors in a shape form, has the function of cutting and tearing food.

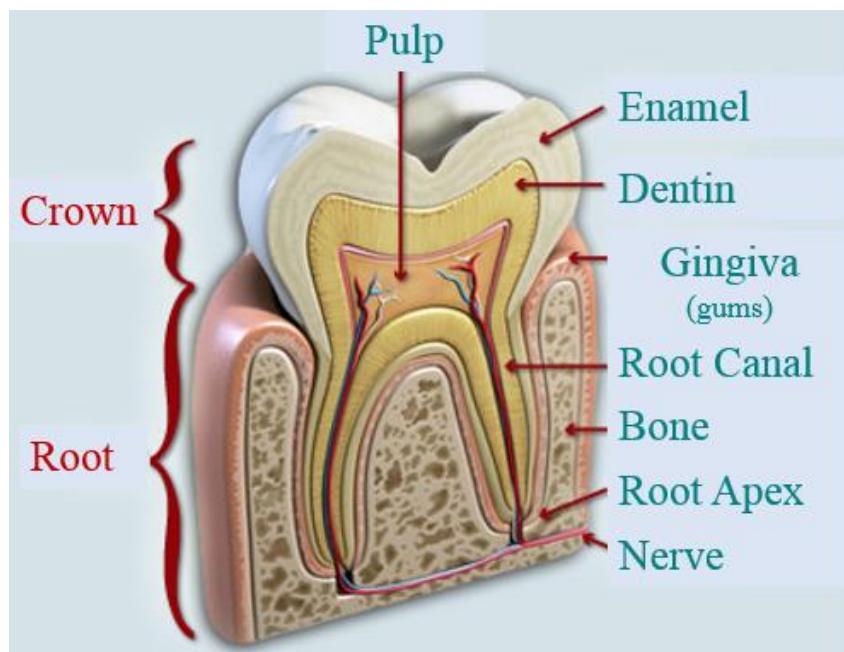
**Premolars (8 total):** Teeth between the canines and molars. Molars have a series of elevations, or cusps, that are used for breaking up particles of food. Behind each canine are two premolars, which can both cut and grind food. Each premolar has two cusps (hence the name bicuspid).

Molars (8 total): The molars by contrast are used exclusively for crushing and grinding. They are the teeth farthest back in the mouth. Each molar typically has four or five cusps.

Wisdom teeth or third molars (4 total): These teeth erupt at around age 18, but are often surgically removed to prevent displacement of other teeth. In humans tends to be variable in size, number of roots, cusp pattern, and eruption. The number of roots for each type of tooth varies from one for incisors, canines, and premolars to two or three for molars.

According to their location, the teeth may be categorized or distinguished in two groups: **anterior** and **posterior** teeth. Central and lateral incisors and canines as a group are called **anterior teeth**; premolars and molars as a group, **posterior teeth**. (Nelson & Ash, 2010).

The tooth has two anatomical parts (Crown and Root) and four tissues (enamel, dentine, cementum and pulp) (Fig 1.2).



<http://www.bradfordfamilydentist.ca/human-teeth-dental-charts/>

**Fig. 1.2** Anatomical parts of tooth (Yanhee Hospital, 2012).

The crown of a tooth is that part of the tooth which is covered with enamel and this the part usually visible in the mouth. The root is the part embedded in the jaw. It anchors the tooth in its bony socket and is normally not visible.

Enamel – The hardest substance in the body, white outer art of the tooth. Enamel is mostly made of calcium phosphate, a rock-hard mineral.

Dentine - not as hard as enamel, forms the bulk of the tooth and can be sensitive if the protection of the enamel is lost. Is made of living cells, which secrete a hard mineral substance.

Pulp – is a connective tissue organ containing a number of structures, among which are arteries, veins, a lymphatic system, blood and nerves. Its primary function is to form the dentin of the tooth.

Cementum – A layer of connective tissue covering the roots of the teeth firmly to the gums and jawbone. It is not as hard as enamel.

Periodontal ligament – Made up of thousands of fibers which fasten the cementum to the bony socket. These fibers anchor the tooth to the jaw bone and act as shock absorbs for the tooth which is subjected to heavy forces during chewing.

Oral mucosa – This is the term used to describe the moist tissue that lines the mouth.

Gingiva (gums) – Soft tissue that immediately surrounds the teeth and bone. It protects the bone and the roots of the teeth and provides an easily lubricated surface.

Bone – Provides a socket to surround and support the roots of the teeth.

Nerves and blood supply – Each tooth and periodontal ligament has a nerve supply and the teeth are sensitive to a wide variety of stimulus. The blood supply is necessary to maintain the vitality of the tooth.

## 1.2 Dental Materials

Dental materials, are materials generally used due the need to replace tooth structure loss, because the presence of dental caries (dental cavities), but also tooth wear and dental trauma. These materials may to maintain or improve the quality of life of the dental patient, preventing disease, relieving pain, improving mastication efficiency and enhancing speech appearance (cosmetics). (O'Brien, 2002, Anusavice, 2006)

The choice of these materials it depends on features such as biocompatibility, bond permanently to tooth structure or bone, match the natural appearance of tooth enamel,

dentin and other tissues and capacity of initiate tissue repair or regeneration of missing or damaged tissues. (O'Brien, 2002). Historically, various materials have been used as tooth crown and root replacements (animal teeth, bone, human teeth, ivory, seashells, ceramics and metals). Actually, dental materials used in dentistry are divided in four groups: metals, ceramics, polymers and composites (Anusavice, 2006).

According (Anusavice, 2006) dental materials may be classified in three categories: *preventive materials, restorative materials or auxiliary materials*.

*Preventive dental materials* – include pit and fissure sealants, sealing agents that prevent leakage (used primarily for antibacterial effects); liners, bases, cements and restorative materials (used primarily because they release fluoride - compomer, hybrid ionomer; glass ionomer cement, zinc silicophosphate cement), chlorhexidine, or other therapeutic agents used to prevent or inhibit the progression of tooth decay (dental caries).

*Restorative dental materials* – all synthetic components that can be used to repair or replace tooth structure, including primers, bonding agents, liners, cement bases, amalgams, resin-based composites, compomers hybrid ionomers, cast metals, metal-ceramics, ceramics, and denture polymers. These materials may be used for temporary, short-term purposes (such as temporary cements and temporary crown and bridge resins) or for longer-term applications (dentin bonding agents, inlays, onlays, crowns, removable dentures, fixed dentures and orthodontic appliances).



<http://www.dentalartslab.com/products-services/implant-prosthetics/fixed-implant-prosthetic-services/>

**Fig. 1.3** Example of restorative materials (Metal and Ceramic).

Restorative materials also may be divided in *direct restorative materials* - used intraorally to fabricate restorations or prosthetic devices directly on the teeth or tissues and *indirect restorative materials* – used extraorally, in which the materials are formed indirectly on casts or other replicas of the teeth and other tissues.

*Auxiliary dental materials* – are substances that are used in the process of fabricating dental prostheses and appliances but that do not become part of these devices (acid-etching, solutions, impression materials, casting investments, gypsum cast and model materials, dental waxes, acrylic resins for impression and bleaching trays, acrylic resins for mouth guards and occlusion aids, and finishing and polishing abrasives).

*Temporary restorative materials* – a subcategory of restorative materials and include products used for dental restorations and appliances that are not intended for moderate-term or long-term applications. This restorative material can be applied for luting, temporary cements, or other restoratives used for fillings, orthodontic wires, and acrylic resins used for temporary inlays, onlays, crowns and fixed and partial dentures (Anusavice, 2006).

### **1.3 Dental Ceramics**

Dental ceramics are an inorganic, nonmetallic solids produced by the heating at high temperatures. Typically consisting of oxygen and one or more metallic or semi-metallic elements (e.g. aluminum, calcium, lithium, magnesium, potassium, silicon, sodium, titanium and zirconium) that is formulated to produce the whole or part of a ceramic-based dental prosthesis.

These materials were categorized by their microstructure, (McLaren & Cao, 2009) which facilitates scientific understanding of the structural and chemical nature of dental ceramics but does little to aid dentists or ceramists in selecting the appropriate material for a given clinical situation. The manner in which a ceramic is processed greatly influences its mechanical behavior and, therefore, its clinical behavior. Therefore, classifying dental ceramics based on their composition and how they are processed can better provide clear clinical parameters for evaluating and appropriately choosing the most conservative ceramic for each clinical situation (McLaren & Whiteman, 2010).

According (Anusavice 2006) ceramics can be classified in four categories: *silicate ceramics*, *oxide ceramics*, *nonoxide ceramics* and *glass-ceramics*.

*Silicate ceramics* are characterized by an amorphous glass phase with a porous structure. The main components are SiO<sub>2</sub> with small additions of crystalline Al<sub>2</sub>O<sub>3</sub>, MgO, ZrO<sub>2</sub>, and/or other oxides.

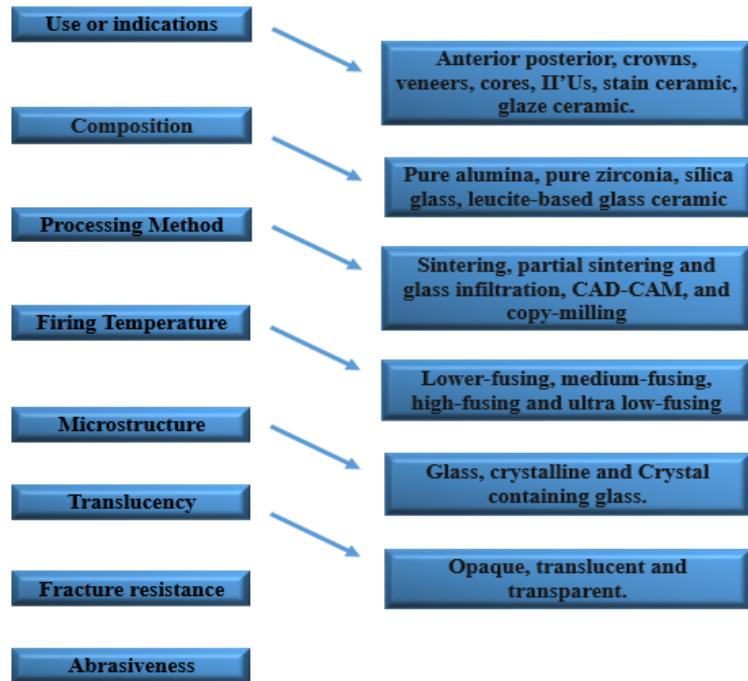
*Nonoxide ceramics* are impractical for use in dentistry, the reasons for their impracticality vary but usually involve either their high processing temperatures, complex processing methods, or unaesthetic color and opacity. Such ceramics include borides (TiB<sub>2</sub>, ZrB<sub>2</sub>), carbides (B<sub>4</sub>C, SiC, TiC, WC), nitrides (AlN, BN, Si<sub>3</sub>N<sub>4</sub>, TiN), selenide (ZnSe), silicide (MoSi<sub>2</sub>), sialon (Si<sub>3</sub>N<sub>4</sub> with Al<sub>2</sub>O<sub>3</sub>), and syalon (Si<sub>3</sub>N<sub>4</sub> with Al<sub>2</sub>O<sub>3</sub> and Y<sub>2</sub>O<sub>3</sub>).

*Oxide ceramics* contain a principal crystalline phase (e.g. Al<sub>2</sub>O<sub>3</sub>, MgO, ThO<sub>2</sub> or ZrO<sub>2</sub>), with either no glass phase or a small content of glass phase. Zirconia is of major dental importance because of its high fracture toughness. Characteristics, morphology, applications of this material will be presented in the following sections of this chapter.

Traditional dental ceramics are mainly multi-phased silicate glass phase ceramics, glasses, glass-ceramics, mono-phased glasses containing various crystal phases or highly crystalline structures (densely sintered alumina and zirconia). (O'Brien, 2002) They all exhibit compositional and microstructural differences, depending on the type of ceramic. Also present chemical, mechanical, physical, and thermal properties that distinguish them from other materials, such as, metals and acrylic resins. The properties of ceramics are customized for dental applications by exact control of the type and amount of the components used in their production.

The dental ceramics are classified according their application in dental laboratories (core ceramic, liner ceramics, margin ceramic, opaque dentin – body or gingival; ceramic, dentin ceramic, enamel – incisal, stain ceramic, glaze ceramic and addition ceramic).

May be also classified in several possible ways, according parameters (Fig 1.4):



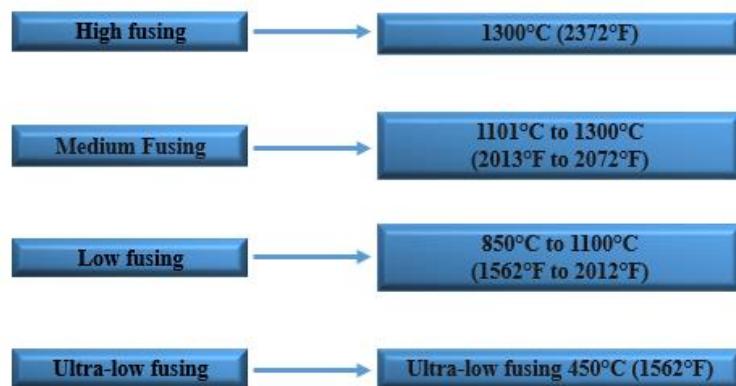
**Fig. 1.4** Classification of dental ceramics.

According type (feldspathic porcelain, leucite-reinforced porcelain, aluminous porcelain, glass-infiltrated alumina, dense alumina, glass-infiltrated spinel, glass-infiltrated zirconia and glass-ceramic), by use (denture teeth, metal-ceramics, veneers, inlays, crowns, anterior bridges, and posterior bridges), by processing method (sintering, casting, or machining), or by substructure material (cast metal, swaged metal, glass-ceramic, CAD-CAM zirconia, or sintered ceramic core) (Anusavice, 2006; Höland et al, 2009a).

Increasing interest has focused on dental ceramic materials, due to their chemical and bio-inertness in the oral environment suitable strength and particularly the fact that these materials are the ones that best mimic the appearance of natural teeth. Dental ceramics are materials that provide the best esthetic characteristics in dental restorations (Heffernan et al, 2002; Sinmazisik and Öveçoglu, 2006; Höland et al, 2009b).

### 1.3.1 Dental porcelains Classification

The classification of dental porcelains in dentistry is apparently an impossible task due to vast improvements made in the compositions. However, these materials can be classified according their applications, fabrication method or crystalline phase (Craig, 2012; O'Brien 2002). According theirs firing temperatures, the dental porcelains are classified as (Fig. 1.5):



**Fig 1.5** Classification of dental porcelain according the firing temperatures.

The medium-fusing and high-fusing types are used for the production of denture teeth. The low-fusing and ultralow-fusing porcelains are used for crown and fixed partial bridges construction (Prado et al, 2002). Actually, are mostly used the low-fusing for dental porcelains.

These transition temperatures are a determinant factor to application of the feldspathic porcelain in clinical dentistry. The porcelain with good mechanical properties, is heat treated at temperature varying 850 to 1100°C in order to cause densification of the material. Another important factor it is the crystallization temperature that can be determines the use of these materials. Generally, sintering and crystallization can occur consecutively or simultaneously. If crystallization occurs before sintering has been completed, the viscosity increases rapidly and the sintering process stops, resulting in a porous material (Prado et al, 2003; Prado et al, 2002). In some situations, however, depending on the heating rate, the sintering process is faster than the crystallization process.

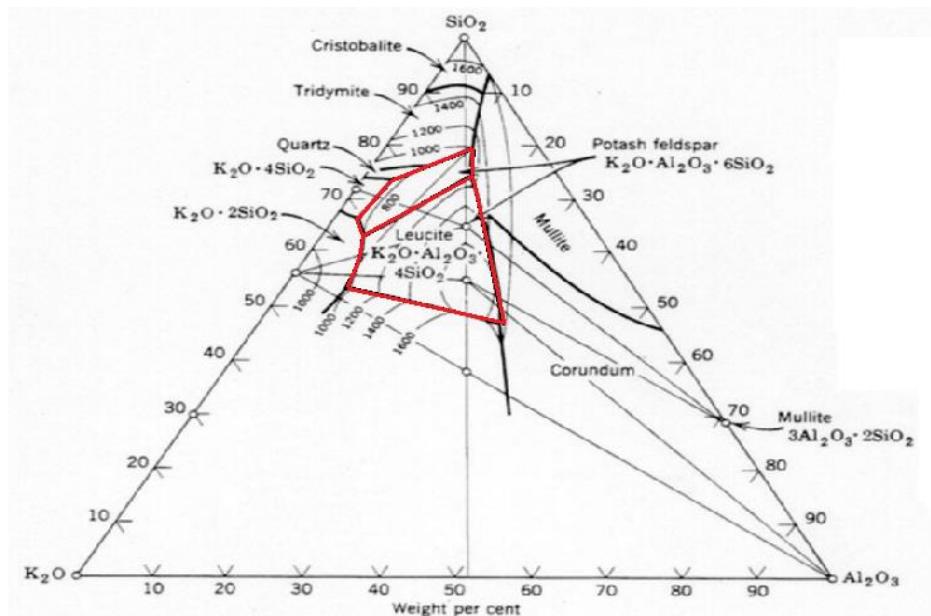
The sintering is the most common process applied to dental porcelains restorations. The process consist of the firing the compacted ceramic powder at high temperature to ensure optimal densification. The densification occurs by pore elimination and viscous flow when the firing temperature is reached. The all-ceramic can also be produced by sintering and use of a wider range of processing techniques such as: slip-casting, heat-pressing and CAD/CAM machining (Craig 2012, O'Brien 2002, Anusavice, 2006).

### **1.3.2 Porcelains Composition**

The quality of any ceramic depends on the choice of components; correct proportioning of each component, and control of the firing procedure. Only the purest components are used in the manufacture of dental porcelains because of the stringent requirements of optical properties and chemical inertness, combined with adequate strength, toughness and thermal expansion. (Fredericci et al, 2011).

The dental porcelains are composed of silica ( $\text{SiO}_2$ ) and alumina ( $\text{Al}_2\text{O}_3$ ) with various amounts of potash and soda feldspar ( $\text{CaO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{B}_2\text{O}_3$ ,  $\text{ZnO}$ ,  $\text{ZrO}_2$ ) for the thermal expansion coefficient of the porcelain. The microstructure of the porcelain consists of a vitreous phase (matrix) and some dispersed/embedded crystalline phases ( $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$  - tetragonal leucite at room temperature) (Fig. 1.6) (Fredericci et al, 2011; Li et al 2005; Tsetsekou et al, 2002;).

The glass matrix present a relatively small percentage of leucite crystal dispersed within it (Giordano, 1996). Kaolin, is a hydrated aluminum silicate  $\text{Al}_2\text{O} \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$  act as a binder, increasing the ability to mold the green porcelain. Thus, for dental porcelains the kaolin was omitted and could therefore be considered a feldspathic glass with crystalline inclusions of silica (Craig & Powers, 2002). The quartz ( $\text{SiO}_2$ ) remains unchanged during the firing process and acts as a strengthening agent. It is present as a fine crystalline dispersion throughout the glassy phase that is produced by the melting of the feldspar. The feldspar fuses when it melts, forming a glass matrix. The feldspar are mixtures of potassium aluminosilicate  $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$  and sodium aluminosilicate, also known as albite  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$  (Clark et al, 2005; Noort, 2002; Barrelro et al, 1989).



**Fig. 1.6** Ternary diagram of  $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ . (Kingery, 1992)

Due to increasing demands for superior esthetics combined with biocompatibility and mechanical performance to withstand the conditions in the oral cavity, dental porcelains may be an interesting alternative to restorative materials in dentistry (Hoque et al, 2015; Magne et al, 2013, Shenoy et al, 2010, Noort, 2002; Fischer et al, 2001, Giordano et al, 1995, Cattel et al, 1997; Philips, 1991; Craig, 1989).

These materials present qualities such as good biocompatibility, aesthetics, compression resistance, high chemical durability, low thermal conductivity (tissue compatible), radiopacity, marginal integrity, color stability similar to natural teeth, translucency, longevity, elevated wear resistance and provides excellent aesthetics that do not deteriorate with time (Chevalier et al, 2004; Rimondini et al, 2002; Leinfelder, 2001;;).

Feldspathic porcelains may be used either alone or associated with a metal or ceramic substructures to construct metal-ceramic/all-ceramic restorations and prostheses. From the development of adhesive cementation techniques, it has been reported in unitary restorations, fixed partial bridges, veneering agents, castable ceramics, porcelain fused to metal restorations and aesthetic facets and inlays/onlays, it is possible to create surface texture glazed similar to individual teeth (Fig. 1.7) (Leinfelder, 2001; Gonzalo-Juan et al 2012; Nakamura et al 2010).



<http://vmcdentallab.com/gallery.html>  
<http://reliablearts.com/portfolio-view/zirconia/>

**Fig 1.7** (a) Metal ceramic and (b) all-ceramic prostheses.

Despite these desirable characteristics, brittle materials such as feldspathic porcelain fail in tension because of their limited ability to absorb a substantial amount of elastic strain energy before fracture. The major problems associate to dental porcelains as tooth replacement materials is their very low fracture toughness (around  $0.7 \text{ MPa m}^{1/2}$ ) and the fact that at a very low strain (0,1%) (Yoshimura et al 2005; Cesar et al, 2006). The density and porosity may affect the mechanical properties of dental porcelain (Fleming et al, 2000). In other words, the ceramic structure only exhibits a very low flexibility before fracture (Jones, 1998).

The dental porcelains are also highly susceptible to strength degradation during their lifetimes in oral environment, because the size of defects tend to increase due to the slow crack growth phenomenon (Yoshimura et al, 2008; Cesar et al 2008; Pinto et al, 2008). Microscopic surface flaws and defects, which may develop as result of thermal, chemical or mechanical process, act as localized stress concentrators.

These applied stresses can cause cracks to originate from the defect sites and propagate leading to catastrophic failure (Albakry et al 2003). Although the compressive strength of dental porcelain is high, its tensile strength is very low, which is typical of a brittle solid that may fracture when flexed or when quickly heated and cooled (Borba et al 2011; Craig & Powers, 2002; Noort, 2002;).

Smales & Etemadi (2004), shown that in porcelain restorations a cumulative survival rate of approx. 60% has been reported for feldspathic onlays without metal reinforcement placed in posterior teeth after 6 years, being bulk fracture reported in 16%

of the restorations. It has also shown a clinical success rate of 64% for maxillary anterior veneers after 10 years. The main reasons for failure were fracture (11%) and large marginal defects (Peumans et al, 2004). For posterior feldspathic inlays, after an 8-year clinical assessment period, marginal and bulk fracture were reported in 22% and 11% of the restorations, respectively (Hayashi et al, 2000; Hayashi et al, 1998;).

Therefore, in order to increase the mechanical performance of porcelain restorations, it is necessary to enhance their overall resistance crack propagation. The understanding of its behavior is the key for the development of materials with longer lifetime (Pinto et al, 2008).

### **1.3.3 Processing**

The dental ceramics technology is one of the areas the most quick increase dental materials research development (Denry & Holloway, 2010). Advanced ceramics represent a significant evolution between the dental applications. The quality of the final ceramic prostheses is dependent on each stage of the fabrication process. Machining or grinding of the core structure is of particularly importance since flaws or cracks can be introduced that could possibly propagate to the point of fracture during subsequent process (Anusavice, 2006).

Dental technicians use a variety of techniques when casting dental porcelains. It is unclear whether these techniques affect the total porosity and shrinkage of dental porcelain (Craig, 1989).

The manufacture of porcelains restorations can be made from various techniques such as: condensation and sintering; drying; shaping under pressure and sintering; casting and sintering; vitreous infiltration and sintering and computer controlled machining (CAD/CAM). The single units crowns can be a metal-ceramic crown (also called a porcelain fused to metal crown), a traditional aluminous porcelain crown based on a core of aluminous porcelain or based on a core of leucite reinforced porcelain (Phillips, 1996).

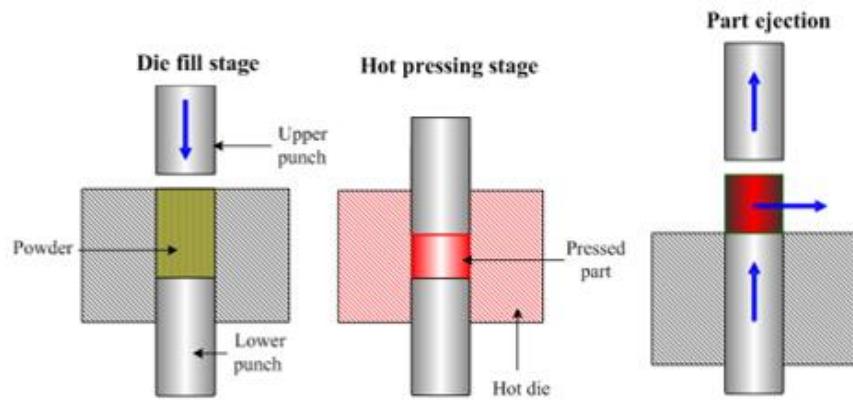
The methods of processing the ceramic core form and ceramic prosthesis are listed (Table 1.1):

**Table 1.1** Techniques of processing and theirs characteristics.

Techniques	Characteristics
Condensation	Ceramic restorations (Dehailan, 2009)
Hot pressing	crowns, inlays, on-lays, veneers and fixed partial dentures (Ven Venkatachalam et al, 2009)
Casting	Porous infrastructure (Crown and bridges) (Denry & Holloway, 2010)
Slip-Casting	Porous infrastructure (Crown and bridges restorations) (Fonseca 2008)
Computer aided machining/milling (CAD/CAM)	Fully sintered ceramic blocks (hard machining) (Duret et al, 1988)
Computer aided machining/milling (CAD/CAM) of pre-sintered form	Partially sintered ceramics (soft machining) (Filser, 2001; Filser et al 2003)

In this thesis, the technique used to prepare porcelain-zirconia composites was hot pressing.

Hot pressing is a technique consists of the application of external pressure to sinter and shape the ceramic at high temperature (Fig. 1.8), and was first used in the fabrication of all-ceramic restorations such as crowns, inlays, on-lays, veneers and fixed partial dentures. Hot pressing, is characterized as avoiding large pores and promoting good dispersion of the crystalline phase within the ceramics and flawless metal-ceramic interfaces and is fulfilled in very fast sintering cycles. Although few, there are some studies on the bond strength of hot pressed porcelain to metal and ceramic dental substructures (Venkatachalam et al, 2009; Drummond et al, 2000, Henriques et al, 2012).

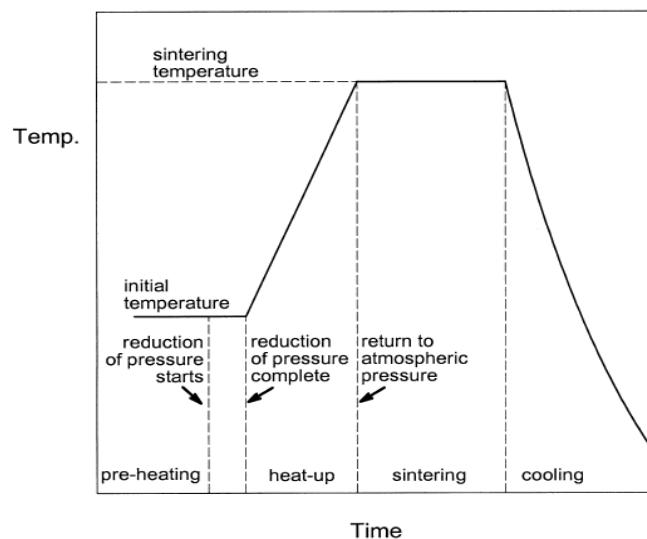


[http://www.substech.com/dokuwiki/doku.php?id=solid\\_state\\_fabrication\\_of\\_metal\\_matrix\\_composites](http://www.substech.com/dokuwiki/doku.php?id=solid_state_fabrication_of_metal_matrix_composites)

**Fig 1.8** Hot pressing process.

### 1.3.4 Sintering Cycles

Sintering is a technique that reduces the porosity of the final product. The first sintering of porcelain is called the **bisque** or **biscuit bake**. After the incisal layer is added, the porcelain is brought to the final stage, called the **glaze bake**. Upon reaching the glazing temperature of the porcelain, a layer of glass is formed on the surface. After glazing, the crown is removed from the furnace and cooled under an inverted glass or beaker. An alternative approach is to add a thin layer of a low-fusing glass or glaze to the surface and fire to the flow temperature of the glaze. The Figure 1.9 shows the firing cycles for dental porcelain.



**Fig. 1.9** Example of sintering cycles for dental porcelain. (Cheung & Darvell, 2002)

The purpose of feldspathic porcelain firing procedures is to densely sinter the particles of powder together and to produce a relatively smooth, glassy layer (glaze) on the surface. In some cases, a stain layer is applied for shade adjustment or for characterization such as stain lines or fine cracks. Several chemical reactions occur over time at porcelain firing temperatures and of particular importance are increases in the concentration of crystalline leucite in the porcelains designed for fabrication of metal-ceramic and all ceramics restorations (Cheung & Darvell, 2002, Swapan et al, 2003; Cheng et al, 2012). The porcelain firing can occur in air or vacuum, depending on the type of furnace.

During the sintering process the pores are reduced, when the air removal. This process create as far as possible a non-porous solid and consequently a porcelain with high strength and aesthetics. Although sintering is often referred to as a solid-state process, here it is driven by surface tension because of partial melting crystalline phases or sufficient softening of glassy material (Frenkel, 1945; Mackenzie, 1949; Herring, 1951;). This reduction of pore volume depends on sintering time (Frenkel, 1945; Herring, 1951;; Ivensen, 1970), temperature (Frenkel, 1945; Herring, 1951;) and atmosphere (Shaler et al, 1948; Vines et al, 1958; Wilson and Whitehead, 1967; Jones and Wilson, 1975; Rosenkranz and Frischat, 1984;,), and the viscosity of the melt (Mackenzie, 1949; Herring, 1951; Bottinga et al, 1972).

In this case, residual stresses can likely accumulate during the heating and cooling firing procedures mainly because of the cooling rate and the coefficient of thermal expansion (CTE) mismatch between core and veneer ceramics (Swain, 2009; Guazzato et al, 2010; Tholey et al, 2010). When additional stresses are applied to the restoration, the probability of failure to fatigue crack propagation might increase (Swain, 2009;; Della Bona et al, 2009; Smith et al, 1994).

In all-ceramics restorations, especially when using the standard layering technique to match the esthetics natural teeth, the multiple firing cycles can be affect the porcelain-zirconia adhesion. Thus, the dental porcelains demonstrate an excellent aesthetics that do not deteriorate with time due to its chemical stability. Because theirs thermal characteristics such as conductivity and coefficient of thermal expansion being similar to dentin and enamel, the porcelains can be employed due the good marginal sealing would prevent percolation related problems (Henriques, 2012).

However, these materials receive amorphous structure that produce physical properties typical of glass, including brittleness and lack of a definite melting temperature. The strength of glasses and brittle materials is highly dependent on porosity (size and number of voids) which act as crack initiation sites by the presence of small flaws or cracks. According the crack propagation theory, when stressed in tension, small flaws tend to open up and propagate, resulting in a low tensile strength. This factor is different when compared as metal (ductile materials) (Anusavice, 2006).

In compression the glasses are much stronger, because compressive stresses tend to close up flaws. Therefore, the tensile strengths of **vitreous** dental porcelains are around (usually between 20 and 60MPa) as compared with compressive strengths of (517 MPa) and very low fracture toughness (<0,1% strain) (Lawn et al, 2001). The strength of dental porcelains is generally tested in flexure as a beam and reported as **modulus of rupture**. The modulus of rupture of a vitreous body or enamel porcelain is about 13,000 psi (90 MPa). In vacuum-fired the strengths of porcelains are higher due to fewer flaws (O'Brien, 2002).

#### 1.4 All-ceramic Restorations

Teeth play a critically important role in our lives. Loss of function reduces our ability to eat a balanced diet, which has negative consequences for health. Loss of aesthetics can negatively impact in social function. Both function and aesthetics can be restored with dental crowns and bridges.

According Höland et al (2009), dental structure loss is related by a variety of factors that range from diseases to trauma, as well as preventable hygiene-related problems. Allied to today's lifestyles, which require a good appearance, this problem has lead to an increasing demand for dental restorations. This demand is translated into an increasing need for dental materials that allow for the creation of teeth esthetically and functionally to natural teeth.

There are many challenges for the physical properties of the ideal dental restorative material. The ideal restorative material would be identical to natural tooth structure in strength, adherence, and appearance.

In this way, ceramics are attractive dental restorations materials because of their aesthetics, biological acceptance, and chemical durability. The all-ceramic dental restorations are domelike structures composed of two layers of materials, namely the reinforcing ceramic core for bearing the biting and the veneer porcelain for aesthetics. However, ceramics are brittle and subject to premature failure, especially under repeated contact loading in a moist environment (Lawn et al, 2001).

Despite a continuous effort in improving the strength of dental ceramics (e.g. using a strong zirconia or alumina core to support a weak but aesthetic porcelain veneer). All-ceramic dental prostheses (including veneered zirconia and alumina restorations) continue to fail at a low rate each year (Burke et al, 2002).

The differences in the fabrication methods used to produce ceramic restorations such as microstructural features, pore and crystal distribution, presence of inclusions and flaws, composition and crystalline content, which could influence the mechanical behavior of materials (Guazzato et al 2004; Guazzato et al,2004a).

In clinical dentistry, it is very important to obtain dental restorations that are as dense as possible, since this will lead to better clinical performance on the long term. Thus, the use of all-ceramic restorations is an interesting step to improve the mechanical properties combined as aesthetics characteristics and replace metal infrastructures (Della Bona & Kelly, 2008).

During the last two decades all-ceramic restorations have become increasingly popular, and, particularly since the introduction of zirconia-based frameworks (Vagkopoulou et al, 2009), a trend toward all-ceramic restorations has been observed.

Zirconia-based ceramics is being proved a successful infrastructure material. Studies have reported no fracture of the zirconia infrastructure in short or medium-term periods of clinical observation (Pjetursson et al, 2008).

The mechanical properties of zirconia enable clinical use of all-ceramic fixed dental prostheses (FDP) even in the molar region (Tinschert et al 2001) and in long span designs (Schmitter et al, 2009). The advantages of zirconia-based substructures are biocompatibility, improved fracture strength and fracture toughness, and their unique

transformation toughening mechanism (Studart et al, 2007). To achieve the best aesthetic results, however, the frameworks must be veneered using ceramics with mechanical properties inferior to those of the substructures and, consequently, the veneering ceramic is the weak part of the system (Al-Dohan et al, 2004; Guazzato et al 2004; Isgro et al, 2003).

The failures in porcelain-zirconia restorations, are frequently associated with biological complications, such as secondary caries, periodontal support and tooth fracture, which likely are not related to the materials used in fixed prostheses (Della Bona & Kelly, 2008; Wang et al, 2014) and some structural deficiencies of the material such as marginal discrepancies, weak performance of the veneering ceramics (Christensen & Ploeger, 2010) and its limited bond to the zirconia substrate (Hübsch et al, 2015; Aboushelib et al, 2009).

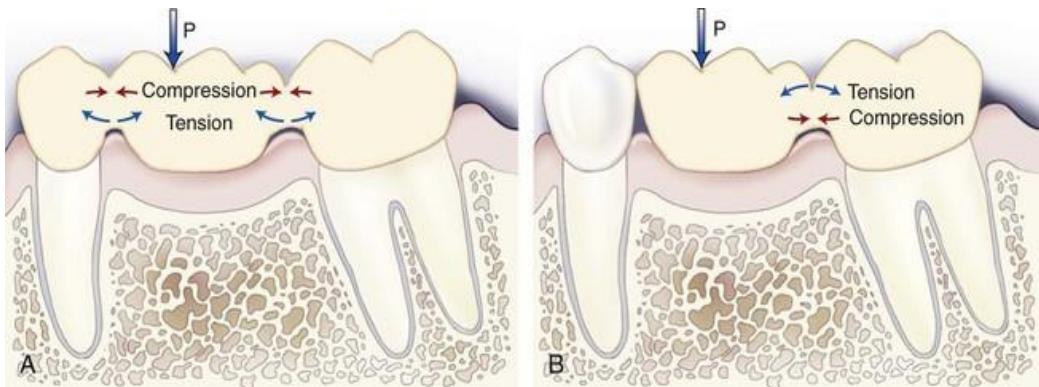
Clinical studies report high survival rates for all-ceramic restorations. Infrastructure failures are unusual when the ceramic material is correctly indicated, varying from 2 to 6% (Al-Amleh et al 2010; Sailer et al 2006, 2007, 2009; Ortorp et al 2009, Suarez et al, 2004).

The failure mode most frequently observed is chipping of the veneering material. This type of failure has been observed mainly when zirconia-based infrastructures are used, showing chipping rates that vary from 0 to 50%, depending on the follow-up period (Al-Amleh et al 2010; Molin et al 2008; Tinschert et al 2008; Sailer et al 2007)). Yet, failure have been described as crack propagation from a contact damage zone throughout the veneering porcelain, reaching or not the interface, which can lead to delamination and exposure of the infrastructure material in the oral environment (Borba et al, 2011).

Swain 2009, shown that residual tensile stresses are create within the porcelain at or near the ceramic-porcelain interface and could contribute to the porcelain fracture in zirconia systems.

Most dental materials are quite brittle; they are highly susceptible to crack initiation in the presence of surface flaws when subjected to tensile stress, such as when they are subjected to flexural loading. The Figure 1.10 shown the stress induced in bridges by a flexural force (P). The stresses are believed to have multifactorial origin, potentially

involving the ceramic thermal history, restoration's geometric factors (i.e. infrastructure design and core-veneer thickness ratio), material's elastic properties "ceramic strength" and poor wetting of the core by the veneer (Guess et al, 2008; De Hoff & Anusavice, 2004-2004a; Benetti et al, 2010). Therefore, these factors should be hand lead carefully to prevent development of high-magnitude tensile stresses.



<http://pocketdentistry.com/mechanical-properties-of-dental-materials-2/>

**Fig. 1.10 A** Stresses induced in a three-unit bridge by a flexural force (P). **B**, Stresses induced in a two-unit cantilever bridge.

Common technical failures in clinical studies on zirconia reconstructions are either the incidence of pure cohesive failure within the ceramic veneer or a mixed failure mode where part of the fracture follow the frame/veneer interface (chipping) (Sailer et al 2006; Tinschert et al 2008).

In both observed failure modes, however, the frame remains intact. This type of failure within the veneering materials is typical in daily clinical practice since load case leading to a destruction of the frame as well, e.g., central axial loading, are associated with force.

Nevertheless, these materials are indicate to produces dental substructures and can be an excellent alternative to replace the natural teeth.

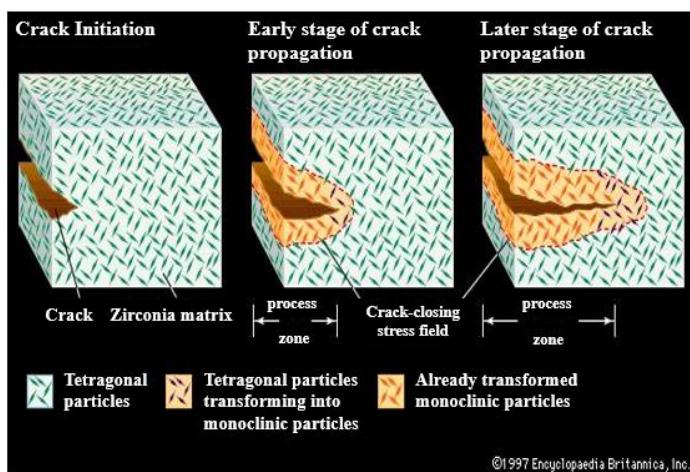
#### 1.4.1 Zirconia

The zirconia ( $\text{ZrO}_2$ ), have received considerable attention in dental applications due to possibility of obtaining substructures and zirconia-based materials with good mechanical properties. This material is considered nowadays one of the most important

ceramic in modern technology due their high mechanical strength and toughness, and good abrasion resistance and chemical stability *in vivo*. (Garvie et al, 1975; Heuer & Hobbs, 1981; Somiya et al, 1988; Hench, 1991; Hannik et al, 2000; Denry et al 2008; Chevalier, 2006).

These ceramics are found in three crystallographic forms: cubic-c (2370-2680°C) to the melting point, tetragonal-t (1170-2370°C) and monoclinic-m from room temperature (30° to 1170°C) (Borchers et al, 2010). Upon cooling from the melting point, zirconia shows two kinds of solid-solid phase transformation, namely, cubic-tetragonal (c-t) (Ackermann et al, 1975; Yoshimura, 1988; Aldebert & Traverse, 1985) and tetragonal-monoclinic (t-m) (Patil & Subbarao, 1969, Subbarao et al, 1974). However, the tetragonal phase is not stable at room temperature, and it can transform to the monoclinic phase with a corresponding volume increase (3-5%) and a shear distortion parallel to the basal plane of t-ZrO<sub>2</sub>.

In general, the tetragonal structure is metastable and presents the major resistance and tenacity (Mechanical strength and fracture toughness ( $K_{IC}$ )) when compared as monoclinic zirconia, and can be explaining due hardening transformations between monoclinic and tetragonal structures (Rauchs et al, 1999). When sufficient stress develops in the tetragonal structure and a crack in the area begins to propagate, the metastable tetragonal crystals (grains) act against the opening of crack, and therefore increase the resistance of the ceramic to crack propagation (Fig. 1.11). These characteristics may be used to increase both the strength and the toughness of zirconia.



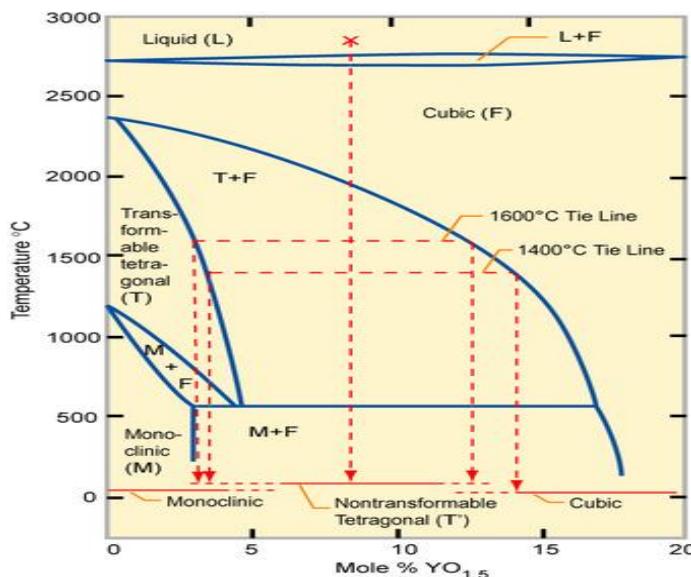
<http://global.britannica.com/science/transformation-toughening>

**Fig 1.11.** Transformation Toughening of Zirconia (Adapted University Cambridge).

The toughening mechanism of crack shielding results from the controlled transformation of the metastable tetragonal phase to the stable monoclinic phase. Several types of crack shielding processes are possible, including micro-cracking, ductile zone formation, and transformation zone formation. This mechanism is significantly extends the reliability and lifetime of  $\text{ZrO}_2$  derived materials and leads to the high fracture toughness of tetragonal zirconia (Garvie & Hannik, 1975).

In order to minimize the effect of volume expansion of zirconia structure (transformation tetragonal to monoclinic), the addition of certain oxides (dimensional stabilizers) is very important (Piconi et al, 1998). These oxides, act as retainers of tetragonal form by addition ( $\text{MgO}$  and  $\text{CaO}$ ) (Yoshimura et al, 2007),  $\text{CeO}_2$  (Ban et al, 2008) and especially  $\text{Y}_2\text{O}_3$  (Atik et al, 1994; Garvie & Hannik, 1975, Chevalier et al, 2004), due to its large solid solubility rage in zirconia, is employed to partially or completely stabilize the tetragonal and cubic structure.

The addition of  $\text{Y}_2\text{O}_3$  (typically 3%) allows decrease the stress, due phases transformations that occurs when cooling of transition temperature between tetragonal and monoclinic phases (thermodynamically stable phase), or also by decrease of particle size above a critic size (Fig 1.12) (Craska et al 2000; Chen et al, 2011; Yashima et al 1996).



[http://www.doitpoms.ac.uk/tplib/fuel-cells/sofc\\_electrolyte.php](http://www.doitpoms.ac.uk/tplib/fuel-cells/sofc_electrolyte.php)

**Fig. 1.12.** Phase Diagram of  $\text{ZrO}_2/\text{Y}_2\text{O}_3$  (University of Cambridge).

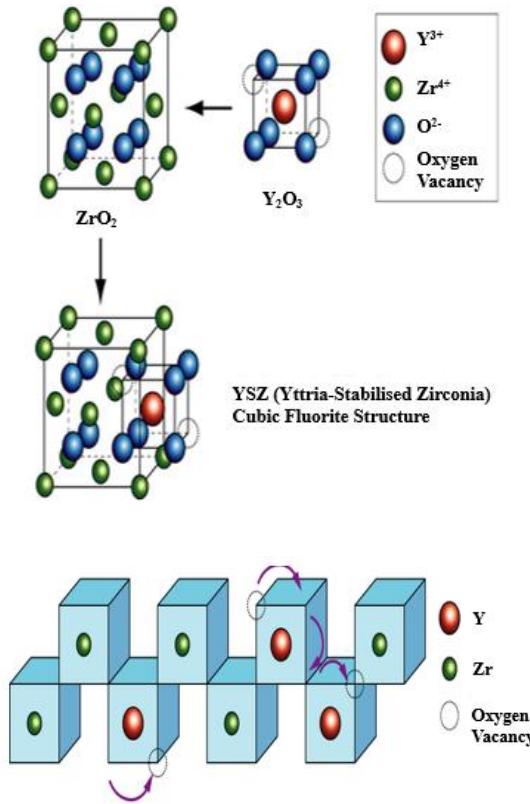
Oxide doping not only modifies the  $\text{ZrO}_2$  structure, but also its vacancy concentration, because a large number of oxygen vacancies is introduced when, for example, divalent ( $\text{Mg}^{2+}$ ) or trivalent ( $\text{Y}^{3+}$ ) ions are incorporated into the zirconia structure for the purpose of phase stabilization. (Yanagida et al, 1996).

The addition of Yttria in pure zirconia, replace some ions ( $\text{Zr}^{4+}$ ) (ionic radius 0,82 Å) into zirconia structure with ions ( $\text{Y}^{3+}$ ), (ionic radius of 0,96 Å). It produces oxygen vacancies, whereas, three ions  $\text{O}^{2-}$  replace four ions of  $\text{O}^{2-}$  (Equation 1).



These vacancies allow that the stabilized zirconia structure lead ions of  $\text{O}^{2-}$  (forming an electrical current), provided there is sufficient local and mobility of this vacancy, this property increase within temperature. The conduction capacity of  $\text{O}^{2-}$  produces the structure stable, such as presented in Fig (1.13) (Yanagida et al, 1996).

In fact, zirconia tetragonal full or partially stabilized present important advantages and they are used in most applications.



[http://www.doitpoms.ac.uk/tplib/fuel-cells/sofc\\_electrolyte.php](http://www.doitpoms.ac.uk/tplib/fuel-cells/sofc_electrolyte.php)

**Fig 1.13** Vacancy transport (Adapted University of Cambridge).

One of the most popular types of doped zirconia used in technologic and biomedical area is Tetragonal Zirconia Polycrystalline (TZP). The TZP combine a pleasant aesthetic appearance with biocompatibility associated to superior mechanical properties (Piconi et al, 1999; Denry et al, 2008).

With this material, it is possible produce a numerous veneering ceramics matching the frameworks of this zirconia as have appeared on the dental market. In powder form, the zirconia act as structural reinforcements, increasing thermal resistance, receive a higher capacity of tenacity of formed surface, high rigidity and high fracture toughness (Moon et al, 2002; Bulgakov et al, 2002).

In dentistry the Y-TZP (Yttria Tetragonal Zirconia Polycrystals) was first introduced to dental clinics in the late 1990s, their microstructure is strong enough to resist the resulting stresses.

This material are the most recent restorations in the dental ceramics family and they have been rapidly adopted for a wide range of applications, because their superior mechanical properties - strong (flexural strength of approximately 900-1200 MPa) and tough (fracture toughness,  $K_{IC}$ , of approximately  $9-10\text{MPa.m}^{1/2}$ ) and achieve good aesthetics results, even without veneering (Benzaïd et al, 2008; Tang et al, 2012; Guess at 2012; Egilmez et al, 2014). Thus, has considerably higher bending and fracture strength than other ceramics (Anusavice, 2006; Guazzato et al, 2004).

The Yttria-stabilized tetragonal zirconia (Y-TZP) have a significant growing in biomedical materials due their superior mechanical properties, chemical stability, high fracture toughness. This material specifically with 3% of Yttria (3YSZ) for theirs characteristics proves to be a suitable material for dental applications, industrial cutters and grinding media (Richard et al, 2000; Chevalier et al, 2009).

Because the material provide high hardness, fracture strength, and structural reliability and show a smaller range of strength variations than porcelain, the yttria-stabilized zirconia ceramic is sometimes referred to as ceramic steel and have higher importance in dental applications (Shijo et al, 2009; Fischer et al, 2008; Anusavice, 2006; Guazzato et al, 2004a).

### **1.4.2 Synthesis of Zirconia**

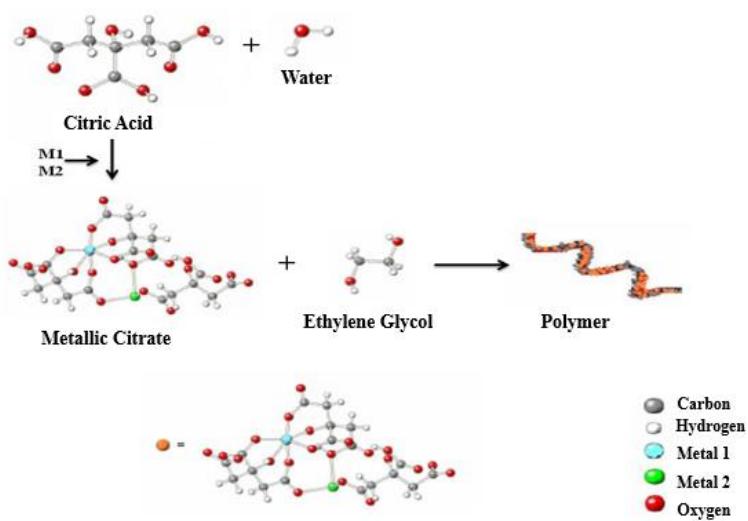
The synthesis optimization to obtain ceramic materials have been crucial and have attracted special attention of the researcher's groups and industry (Li et al, 1994). This interest has resulted in substantial increase from the development and production of the nanostructured materials, improving the functionally characteristics when compared as conventional ceramics (Duncan et al, 2006).

In this context, the zirconia powders are obtained generally by solid state reactions at high temperatures (Li et al, 2001; Politova et al 2004) or by wet methods such as: hydrolysis (Rauchs et al, 1999; Yang et al, 1997), sol-gel method (Kessman et al, 2009; Matsui and Ohgai, 2000), precipitation (Vargas et al, 2003; Atkinson e Segal, 1998), hydrothermal synthesis (Aruna et al, 2011; Masala et al, 2006) and complex polymerization method (CPM) (Razpotnik and Macek, 2007; Grzebielucka et al, 2010).

From the exposed methods above, the Complex Polymerization Method (CPM) presents advantages such as: easy synthesis process, good chemical homogeneity, high purity, stoichiometric control, nano-metric powders, low processing temperature and cost (Cunha et al, 2005). This method, comprises in polymeric resin formation originated by polyesterification process between metallic cations complexed (chelates using hydroxycarboxylic acids) and a polyalcohol such as ethylene glycol (Pechini, 1967).

The CPM method provides a chemical way to distribute evenly the metallic ions in a polymeric resin in atomic scale (Landeros et al, 2009). During the synthesis process occurs the cations distribution at the molecular level in polymer structure. The heating around 90°C, in air atmosphere, promotes the condensation reaction (alcohol and acid chelate), with the rise of water molecules, then occurs the polyesterification and the excess water is removal by evaporation, emerging a polymeric resin at solid state to rear powders achievement (Quinelato et al, 2001). The decomposition of polymeric resin is necessary to eliminate of the organic compounds by heat treatment, obtaining the desired phase.

Besides, it is a flexible method, being directed in obtaining of various oxides, and distinct structures modified from the parameters adjustment (Cushing, 2004). The figure 1.14 shown the reactions of the Complex Polymerization Method.



**Fig 1.14.** Complexation reaction and polymerization in the CPM. (Motta, 2008).

The organic material elimination is possible from the calcination to obtain the desired phase. The calcination temperatures ( $300^{\circ}\text{C}$ ) promote the polymeric chains rupture and the combustion of the material (pyrolysis). In temperatures between  $300^{\circ}\text{C}$  and  $900^{\circ}\text{C}$  occurs the metallic cations oxidation (crystallites of oxides) (Motta, 2008).

One of the disadvantage of this method consist in a small control of particle size, format and morphology. Unlike the sol-gel method when the metal it is a constituent part of the gel network, in the CPM the synthesis is formed by chelating agent polyesterification to a mono-hydroxylic alcohol (Cushing, 2004; Galvão, 2010).

Thus, occurs imprisonment of metallic ions in the organic compounds with weak bonds. Also presents the large weight loss, forming agglomerates during the calcination process, due the additional heating produced by material calcination and combustion (sintered agglomerates) (Cushing, 2004).

## **1.5 Particulate Composites**

A composite material can be defined as a combination of two or more materials that results in better properties than those of the individual components used alone. Differently to metal alloys, each material retains its separate chemical, physical, and mechanical properties. The two constituents are a reinforcement and a matrix (Campbell, 2010, Callister, 2004).

Ceramics and ceramic composites are promising materials having high strength characteristics but quite low crack resistance properties at the same time. This is one of the major factors hindering the wide-scale application of these materials in various fields of human activities. The main advantages of composite materials are their high strength and stiffness, combined with low density, when compared with bulk materials, allowing for a weight reduction in the finished part (Chawla 1998).

The crack resistance is critical not only for ceramic products operating under extreme mechanical and thermal loads but also for structural components whose brittle fracture is intolerable even under arbitrary loads (Gogotsi, 2002).

Effect of the dispersed particles on the composite properties depends on the particles dimensions very small particles (less than 0.25 micron in diameter) finely distributed in the matrix prevents movement of dislocations and deformation of the material. Such strengthening effect is similar to the precipitation hardening.

The dispersed phase of particulate composites (ceramic particles) is usually stable at high temperatures, so the strengthening effect is retained. Many of composite materials are designed to work in high temperature applications. The reinforcing phase present strength and stiffness properties. Generally, the reinforcement is harder, stronger, and stiffer than the matrix. The reinforcement can be a (fiber or a particulate) (Campbell, 2010).

### *Particulate composites*

Particulate composites consist of a matrix reinforced with a dispersed phase in form particles. They may be spherical, platelets, or any other regular or irregular geometry. Particulate composites tend to be much weaker and less stiff than continuous fiber composites, but they are usually much less expensive. Particulate reinforced composites usually contain less reinforcement (up to 40 to 50 volume percent) due to processing difficulties and brittleness (Campbell, 2010).

Generally, these materials with improved properties, are compared with “pure” matrix materials to understanding the mechanisms that occurs during the fabrication process. Properties of particulate composites depend on: Concentration, size, shape, distribution and orientation this factors can achieve a significant improvement of hardness, stiffness, fracture toughness and/or strength of the material. It was also reported that the decrease of inclusion size to the nanometric scale allowed extremely high values of flexural strength and fracture toughness to be achieved. (Campbell, 2010)

The manufacturing of composites with ceramic matrix almost always leads to residual stresses caused by the mismatch of thermal properties of constituent phases. The difference in thermal expansion coefficients (CTE's) could introduce stresses reaching even hundreds of MPa to the composite system. Such a phenomenon to influence fracture toughness of the material (Grabowski & Edzich, 2007).

These composites are designed to produce unusual combinations of properties rather than to improve the strength (Hull, 1996). Mechanical properties, such as elastic modulus, of particulate composites achievable are in the range defined by **rule of mixtures** as follows Equations. (2 and 3):

Upper bound is represented by:

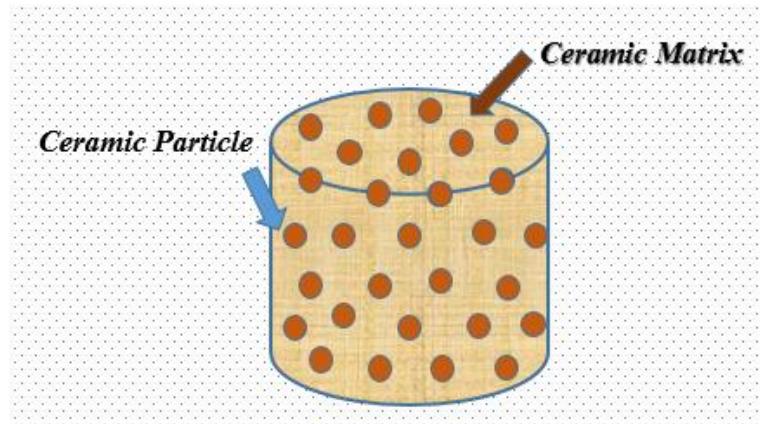
$$E_c(u) = E_m V_m + E_p V_p \quad (2)$$

And lower bound is represented by:

$$E_c(l) = \frac{E_m E_p}{E_p V_m + E_m V_p} \quad (3)$$

Where:

$E$  – elastic modulus;  $V$  – volume fractions;  $c, m, p$  – present composites, matrix and particulate phases, respectively. A schematic diagram of these bounds is shown in the Fig. 1.15.



**Fig. 1.15** Particulate reinforced composite.

In dentistry the use of particles as reinforcement in porcelain matrix is widely applied to increase the mechanical properties of these composites. The possibility of some improvement of mechanical properties of oxide ceramics by manufacturing of particulate composites has been very well recognized recently. (Gogotsi, 2002)

The tetragonal zirconia ceramics show a relatively good reliability and widely used as reinforcement in metals and ceramics matrix. A typical value of the Weibull parameter ( $m$ ) for TZP is about 20. However, not many data describing the reliability of particulate composites with TZP matrix are available. It is expected microstructure of the composite influences the material reliability (Madfa et al, 2014). Thus, the final properties of these composites can be influenced by correct choice of the some parameters such as amount of inclusion; their size and dispersion are decisive for the final values of mechanical properties of the material.

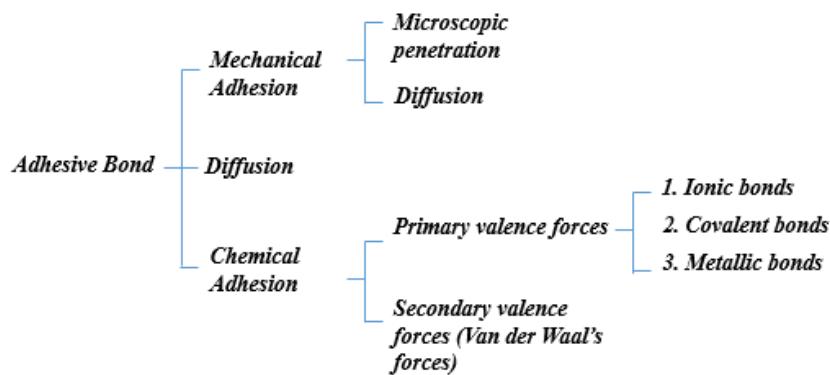
## 1.6 Ceramic-ceramic composites interaction/Adhesion

The adhesion is the attachment of materials in contact that resists the forces of separation. Adhesive phenomena are critical in many areas of dental materials, including the bonding of porcelains to metals and the adhesion of resins to tooth structure (O'Brien, 2002).

Several types of adhesive bonds may be identified according to the classifications. Mechanical adhesion depends on mechanical interlocking of the two phases and may include microscopic attachments, as in the case of resin bonding to etched enamel or hoop stresses of a porcelain around a metal core. Chemical adhesion relies on chemical bonding between two phases. Diffusion bonding results when one phase

penetrates by diffusion into the surface of a second phase and forms a hybrid layer, which is a composite of the two materials (Lewis & Natarajan, 1975; Anusavice 2006).

The classification of bonding mechanisms can be draw (Figure 1.16):



**Fig. 1.16** Classification of Bonding Mechanism (O'Brien, 2002)

Several factors affect the strength of an adhesive bond:

- *Cleanliness*. The surfaces to be attached should be free of debris and contamination.
- *Penetration of surface*. Liquid adhesives (e.g., sealants and bonding agents) must penetrate into crevices created by acid etching of enamel and dentin. The penetration coefficient of the liquid was discussed in the preceding section.
- *Chemical reactions*. The formation of strong chemical bonds across an interface will increase the number of attachment sites. This is believed to occur between porcelain enamels and the oxides of tin, indium, and iron formed on the surfaces of alloys containing high proportions of precious metals. On the other hand, a weak compound may be formed by a chemical reaction, resulting in a weak boundary layer (e.g., certain oxides) rather than attachment sites.
- *Shrinkage of adhesive*. Liquid adhesives solidify by processes such as solvent evaporation and polymerization, and shrinkage results. The adhesive may then pull away from the substrate, or stresses may be created that weaken the bond.
- *Thermal stresses*. If the adhesive and substrate have different thermal expansion

coefficients, changes in temperature will produce stresses in the bond. For example, porcelain enamels are bonded to alloys at high temperatures and then cooled to room temperature. Close matching of the thermal expansion coefficients of porcelain enamel and alloy is required to minimize stresses.

- *Corrosive environment.* The presence of water or corrosive liquid or vapor will often lead to deterioration of an adhesive bond. For example, acrylic resins will initially adhere to clean unetched tooth enamel, but the bond deteriorates upon storage in water.

The studies of adhesive bonding started by Buonocore in 1956, has evolved through many generations in which adhesives have become stronger, easier to use, and have important for dental applications (Buonocore et al, 1956).

In dentistry, the ceramic-ceramic bonding specially yttria-stabilized tetragonal zirconia polycrystal (Y-TZP) with porcelain, has been widely used in the production of all-ceramic restorations nowadays, the relatively higher failure rate of zirconia-based prostheses compared with porcelain-fused-to-metal (PFM) restoration is still concerned (Guess et al, 2008, Sailer et al, 2007).

The weak bonding might be due to some factors, a mismatch in the coefficients of thermal expansion (CTE) of the core and veneer ceramics and its resulting pre-stresses, transformation of zirconia crystals at core-veneer interface, due to thermal influences or stress loading (interface toughness) surface treatment, lack of chemical bonding, unintentional formation of micro-porosities at the interface. (Aboushelib et al, 2006; 2008)

These factors, has been stated that the success of all of veneer/core bilayer restorations depends on the mechanical adhesion between veneering ceramic and zirconia core (Raigrodski et al, 2006). Several studies (Ozcan & Vallittu, 2003; Kern et al, 2009; Al-Amleh et al, 2010) have investigated the bond strength and the durability of various bonding methods to dental ceramics. Nevertheless, there is a little information about the bond quality between veneering ceramic and zirconia core (Ozkurt et al 2010; Chaiyabutr et al, 2008).

In oral environment, the good core-veneer bond strength is a clinical requirements to avoid premature failure of all-ceramic restorations (Aboushelib et al, 2009).

### 1.6.1 Bond Strength Tests

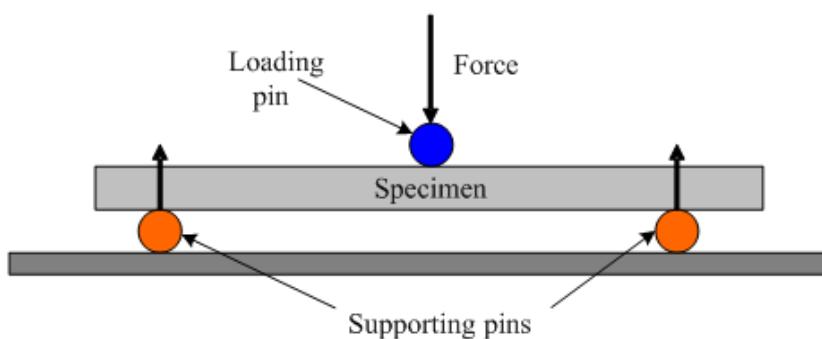
To evaluate the ceramic-ceramic unions some tests are used, and are classified as flexural strength or shear strength (Chevalier et al, 2009; Jung et al, 2000).

In brittle materials the normal tensile test cannot easily be performed because of the presence of flaws at the surface. The lower concentration increase the probability of failure and uniform distribution of stresses in microspecimens, in this case, holding microtest is needed to asses theses parameters (Chevalier et al, 2009; Jung et al, 2000).

Often, just placing a brittle material in the grips of the tensile testing machine causes cracking. These materials may be tested using the bend test. (Engineering Archives, 2012).

The flexural strength present two configurations: three or four point loading (Lavine and Custer, 1996; O'Brien and Craig, 1977). For these type of materials the ISO 6872 it is most appropriate. The ISO 6872 specifies the requirements and the corresponding test methods for dental ceramic materials for fixed all ceramic and metal-ceramic restorations and prostheses. The flexural strength testing specifications, provided by ISO 6872 include but are not limited to ceramic dental fillings, crowns, veneers, implants, and brackets.

In this test, the rectangular specimens or flat cross-section is placed on two parallel supporting pins. The load is applied in the center with the ceramic surface down until failure of the ceramic occurs (Figure 1.17).



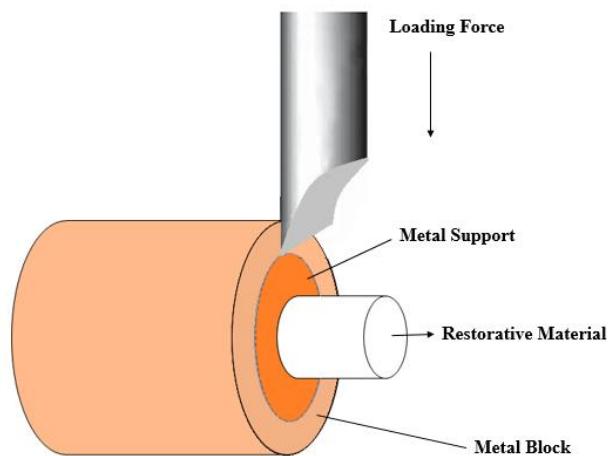
[http://www.substech.com/dokuwiki/doku.php?id=flexural\\_strength\\_tests\\_of\\_ceramics](http://www.substech.com/dokuwiki/doku.php?id=flexural_strength_tests_of_ceramics)

**Fig. 1.17.** Three point bending of a ceramic specimen according to ISO 6872.

This configuration provides uniform loading of the specimen and prevents friction between the specimen and the supporting pins.

The shear bond strength is another test used to identify the adhesive parameters in ceramic-ceramic materials. This tests is indicate due to criticism because the maximum tensile stresses that are created at the surface porcelain, this resulting in predictable tensile failures (Anusavice et al, 1980; McLean, 1980).

Generally, has been used the planar interface shear bond test (DeHoff et al, 1995). The planar interface shear bond tests are bond tests with porcelain applied to a flat zirconia surface. The ceramic-ceramic bond sites can be circular or rectangular. The tests intends to separate porcelain from zirconia substrate (Fig. 1.18).



**Fig. 1.18** Shear bond test for restorative materials.

The ISO 29022:2013 is the standard normally used for dental materials. The ISO 29022:2013 specifies a shear test method used to determine the adhesive bond strength between direct dental restorative materials and tooth structure, e.g. dentine or enamel.

The method as described is principally intended for dental adhesives. The method includes substrate selection, storage and handling of tooth structure. Can be applied for all-ceramic restorations. These tests reproduce the realistic conditions and generates information that is useful to better predict clinical reliability of ceramic-ceramic dental systems (De Hoff et al, 1995).

## 1.7 Clinical Applications of dental Porcelain

In recent years, the dental porcelain has found an increased number of applications from the development of new methods for the construction of porcelain veneers, intra-coronal restorations, jacket crowns, metal ceramic crowns and posterior/anterior bridges.

Porcelain laminate veneers were initially described by Horn 1983. It is fitted to the surface of prepared enamel by a combination of mechanical bond to etched enamel is by means of a composite resin (Hussin, 1979)

Porcelain Jacket Crown or All-porcelain Crown system. Porcelain jacket crowns have been used widely in dentistry since Land developed the platinum foil technique in 1903. The feldspathic porcelains were known for natural esthetics resulting mainly from high translucency and the specialized laboratory skills used (Anusavice, 2006) (Fig 1.19). Therefore, because the presence of microcracks and tendency to fracture, almost all porcelains are strengthened with alumina crystals incorporated into the porcelain powder (McLean and Hughes, 1965).



<http://www.affinitydentalclinics.com/dentalservices/dental-crowns-jacket-crown/>

**Fig 1.19.** Porcelain Crown.

Porcelain bonded to metal restorations. It is composed of a porcelain facing bonded to the surface of the metal substructure or coping, which fits over the tooth preparation. Bonding of porcelain to metal alloy during firing is achieved by Mechanical interlocking, Chemical or molecular bonding and Van der Waals forces (Vickery 1968, Bardirelli 1968, Cascone 1977, McLean 1979, Bagby et al. 1990).

Ceramic inlay/onlay. There are two ceramic inlay systems, the first is laboratory made, in which the porcelain inlay is fabricated by condensing porcelain into a refractory

die which replicates the prepared tooth, while the second is a chairside system which involves milling of a porcelain inlay which is designed in a computer form a three-dimensional video image of prepared tooth (Smith, 1990). All porcelain bridges are not yet widely accepted restoration. Al-Ajlouni et al 2004) stated that all-porcelain resin-bonded bridges, especially the veneer type, can doubtfully sustain forces in the mouth. Some authors mentioned that porcelain bridges can be reinforced through the incorporation of a rod of recrystallized alumina into the structure. The porcelains also widely used in dental implantology (Al-Ajlouni et al, 2004).

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ISO 29022:2013 <https://www.iso.org/obp/ui/#iso:std:iso:29022:ed-1:v1:en>

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## **CHAPTER II**

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### **Comparative study between commercial zirconia and zirconia synthesized with different Yttria contents and calcination temperatures by Complex Polymerization Method (CPM).**

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#### **Abstract**

The aim of this study was to accomplish a previous characterization of the zirconia synthesized by Complex Polymerization Method (CPM) using different yttria content (3, 4, 5 mol. %) and calcination temperatures and compare these results with commercial zirconia. The powders were crystallized at 800, 900 and 1000 °C for 2h. The structural evolution Y-TZP powders were characterized by X-Ray Diffraction (XRD) and Micro-Raman Spectroscopy. The thermal properties of the calcined pre-pyrolyzed (350 °C for 4 h), samples were investigated by simultaneous thermoanalysis (TGA/DTA). After heat treatment the phase Y-TZP was obtained of a single-phase, with absence of the deleterious phases. The results show that average crystallite size of the powder synthesized with 3% of Yttria dopant, increased from 11.5 to 27.9 nm when the calcination temperature increased from 800 to 1000°C. This behavior was observed for all specimens independent of the Yttria content. Commercial zirconia show the average crystallite size to order 37.0 nm. The weight loss for synthesized specimens (3, 4 and 5 mol %) is major than compared with commercial zirconia, 85, 72, 86 and 2%, respectively. The micro-Raman indicate the presence of the tetragonal phase for all samples independ of the composition and calcination temperature employed.

**Key-words:** zirconia, yttria, synthesis, Complex Polymerization Method (CPM).

## **1. Introduction**

Zirconia ceramic materials are widely and increasingly used in dentistry due to their outstanding biocompatibility and aesthetics (Jing et al, 2014). This material is one of the most employed technical oxide ceramics, especially when partially stabilized with a suitable amount of yttrium oxide. Tetragonal zirconia polycrystals with 3 mol% of yttria (3Y-TZP) have a metastable tetragonal structure at room temperature and exhibit very high tensile strengths thanks mostly to their sub-micron grain size and moderate fracture toughness (Viazzi et al, 2008; Kazemi et al, 2011).

The 3Y-TZP can be used to fabricate multiunit fixed partial dentures (Piconi et al, 1999; Borchers et al, 2010), inlays (Piconi et al, 1999; Thompson and Rekow 2004; Meyenberg et al, 1995) and implants (Kohal et al, 2013) due to its excellent mechanical, thermal, and tribological properties, biocompatibility and corrosion resistance (Chevalier et al, 2009).

From the need to improve the functional characteristics of the nanostructured ceramic materials compared as conventional ceramic, the development and production of these materials was expanded (Duncan et al, 2006). In nano scale, the zirconia powders receive various advantages, especially at high temperatures such as: low thermal conductivity, sintering temperature reduced, improvement on mechanical properties and superplasticity (Somiya et al, 1986; Skandan et al, 1994).

Zirconia powders with different dopant contents can be produced by various methods such as solid-state reactions at high temperatures (Li et al, 2001; Politova et al 2004) or via wet synthesis method hydrolyses (Rauchs et al, 1989; Yang et al, 1997), sol-gel (Kessman et al, 2009; Matsui et al, 2000), co-precipitation (Atkinson et al, 1998; Vargas and Goto, 2003), high energy milling (Masala and Seshadri, 2004), Hidrotermic method (Politova et al, 2004; Aruna and Rajam, 2004) combustion processes (Venkatachari et al, 1995), complex polymerization (Hajizadeh-Oghaz et al 2014), has being applied to synthesize different types of ZrO<sub>2</sub> nanopowders.

Serious problems in processing zirconia-based solid solutions resulted from these high-temperature techniques, including uncontrolled grain growth, deep segregation of dopant and possible loss of stoichiometry due to the volatilization of a reactant at high temperatures (Salavati-Niasari et al, 2009). For this reason, based on wet chemical routes, several increasingly important alternatives make the synthesis of zirconia-based solid solutions at mild temperatures possible.

Thereat, the CPM (Complex Polymerization Method) has demonstrated the potential choice to synthesize zirconia powders. In this method, these problems are reduced because the synthesis occurs at a low temperature and the immobilization of the metal complexes in such rigid organic polymeric networks can reduce the metal segregation, thus ensuring the compositional homogeneity at the molecular scale. A poly alcohol such as ethylene glycol (EG) is added to establish the linkages between the chelates by a polyesterification reaction, resulting in the gelation of there action mixture. By gel calcination, nanocrystalline powders were obtained (Sakka and Kozuka, 2005; Hajizadeh-Oghaz et al 2013). Besides, is a low cost method when compared to others techniques, easy to obtain, synthesis parameters controlled, facilitating the synthesis of materials with appropriate characteristics (Motta et al, 2008).

Therefore, this work aims to compare the influence of Yttria content in zirconia assigned by Complex Polymerization Method (CPM) with commercial zirconia and discuss the relationships between processing parameters and calcination temperature employed. These results can help to understand about the better materials to manufacturing zirconia susbstructures for dental applications.

## 2. Experimental Procedure

### 2.1 Materials

In Table 2.1 are presented the precursors for Zirconia doped with yttria by CPM and commercial Zirconia.

**Table 2.1.** Reagents used to obtaining the zirconia powder by CPM.

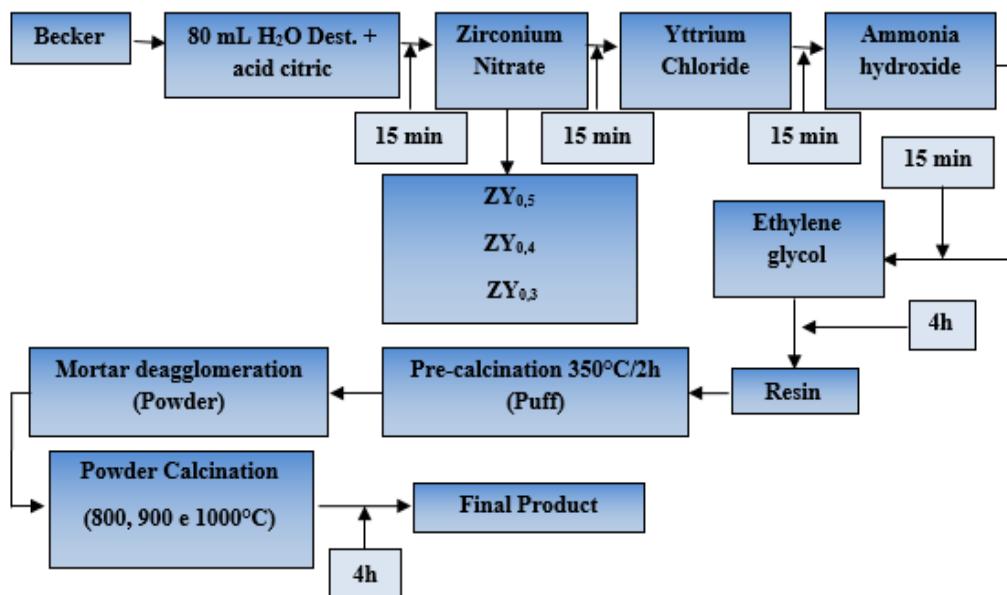
Reagents	Molecular Formula	Supplier	Purity (%)
Zirconium Nitrate	ZrO(NO <sub>3</sub> ) <sub>2</sub> .3H <sub>2</sub> O	Aldrich	99,0
Yttrium Chloride Hydrate	Y(Cl <sub>3</sub> ).6H <sub>2</sub> O	Aldrich	99,9
Citric Acid	C <sub>6</sub> H <sub>8</sub> O <sub>7</sub>	Vetec	99,5
Ammonium hydroxide	NH <sub>4</sub> OH	Aldrich	99,0
Ethylene Glycol	C <sub>2</sub> H <sub>4</sub> (OH) <sub>2</sub>	Synth	99,0
Commercial Zirconia	97% ZrO <sub>2</sub> and 3% Y <sub>2</sub> O <sub>3</sub>	Tosoh	98,0

## 2.2 Methods

The samples of zirconia in molar proportions (3, 4, and 5 mol %) were synthetized and named as ( $ZY_{0,3}$ ), ( $ZY_{0,4}$ ), ( $ZY_{0,5}$ ) and commercial zirconia (CZ), respectively. The Figure 2.1 show the flowchart of the zirconia synthesis by CPM. A solution was prepared in a Becker (80mL) of destiled water and citric acid (complexing agent) (202g/mol). The formed solution stayed stirring at 65-70°C for 15min.

Then, was added the Zirconium Nitrate ( $ZrO(NO_3)_2$ ) (231,23g/mol) and with homonegeity of solution was added the yttrium chloride ( $Y(Cl_3)_6H_2O$ ) (195,26g/mol) (stabilizing volumetric). After, was added the ammonia hydroxide (25mL) to fit the pH = 8 e finally, the ethylene glycol (25mL). The solution volume was reduced during a period of 4h, forming a resin (dark color). The resin was pyrolysed at 350°C/2h by “puff” formation. This puff was deagglomerade in agata mortar and the powder was calcined at 800, 900 and 1000°C and a reating rate at 10°C/min for 4h to all stoichiometric proportions ( $ZY_{0,3}$ ), ( $ZY_{0,4}$ ), ( $ZY_{0,5}$ ).

This synthesis process was accomplished according the relation citric acid/metallic cations in proportion 3:1 mols. The amounts of acid citric, ammonium hidroxide and glycol etilene was stoichiometrically established following the relation citric acid/metallic cations.



**Fig. 2.1.** Flowchart of the zirconia synthesis by CPM.

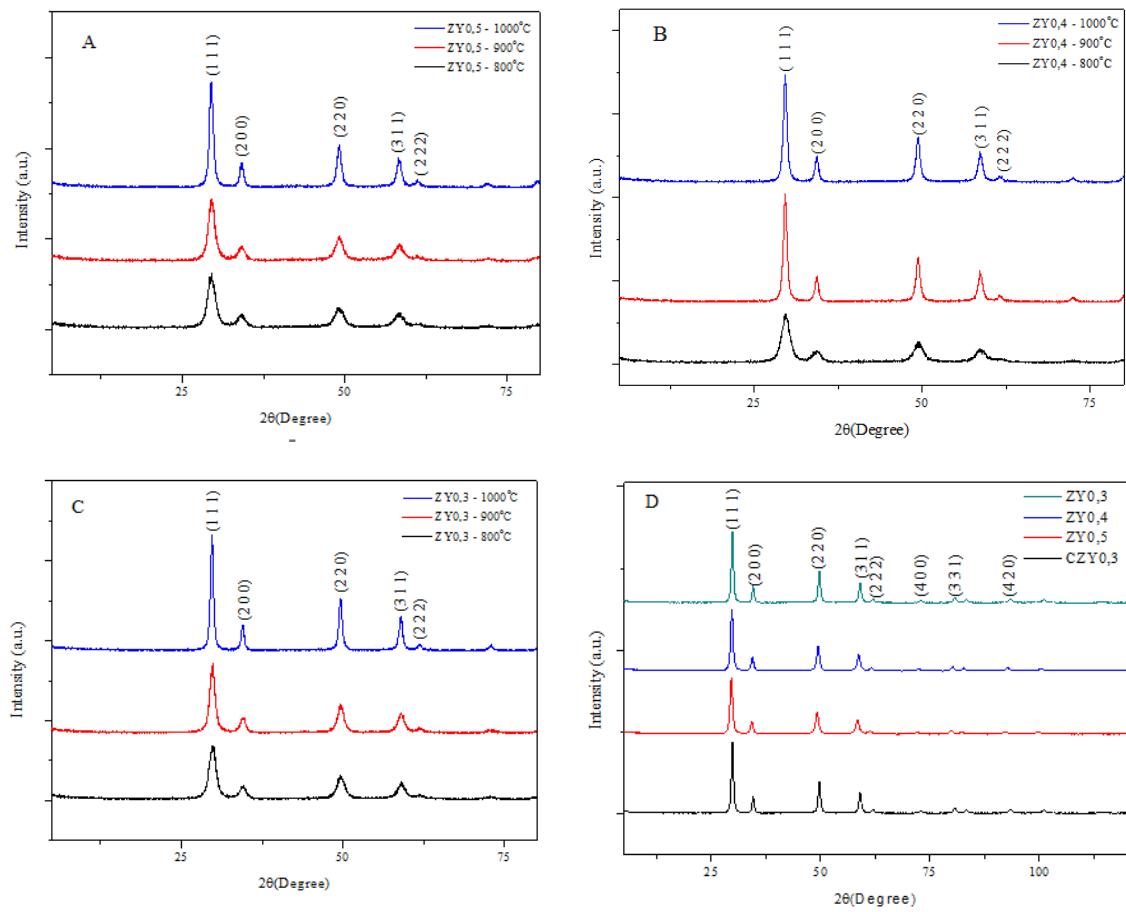
## 2.2.2 Characterizations

The Crystal structures were identified by a powder X-ray diffractometer (XRD, SHIMADZU XRD 6000) employing Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). Powder crystallite size was determined with X-PAS software using the Scherrer equation and X-ray diffraction line broadening of (1 1 1), (2 2 0), (3 1 1) peaks for Yttrium doped zirconia.

The thermoanalyses were held using the powder material in a sample-port inserted (1:1) into of the capsule for characterization with N<sub>2</sub>/O<sub>2</sub>/Air. The parameters used were the same held for specimens calcined, the heating rate at 10°C·min<sup>-1</sup> and the temperature evaluate at 1100 °C. The Raman spectra was obtained at room temperature using a RFS/100/S Bruker FT-Raman equipment over the scan range of 100–1400 cm<sup>-1</sup>, using the 1064 nm exciting wavelength of a Nd:YAG laser.

## 3. Results and Discussion

XRD patterns of the synthesized powders by CPM with different Yttria contents (3, 4 and 5 mol. %) are shown in Fig. 2.2. The specimens were calined at 800, 900 and 1000 °C for 4h. The figures show the most intense (1 1 1) peak in the X-Ray diffraction patterns recorded to all calcination temperatures for zirconia powders with 3, 4 and 5 mol. % of the Yttria content (Fig. 2.2. A, B and C), respectively. This same behavior (cubic phase), due the crystallographic similarity between “a” cubic structture (cfc) and tetragonal structure, promote this identification trouble (Fig. 2.2D). The operating temperature considered was (1000 °C) for specimens synthesized in comparison as commercial zirconia. In this diffractogram the scan angle is slightly higher (120°), to try found the tetragonal phase. X-Ray diffraction indicates the presence of majority cubic phase (JCPDS N° 77-2113) for all calcination temperatures and applied stoichiometry.



**Fig 2.2.** XRD for specimens with varied Yttria content in zirconia (A, B and C) and comparative XRD between zirconia with Yttria content (5, 4 and 3% at 1000°C) and commercial zirconia – CZ with 3% of Yttria (D).

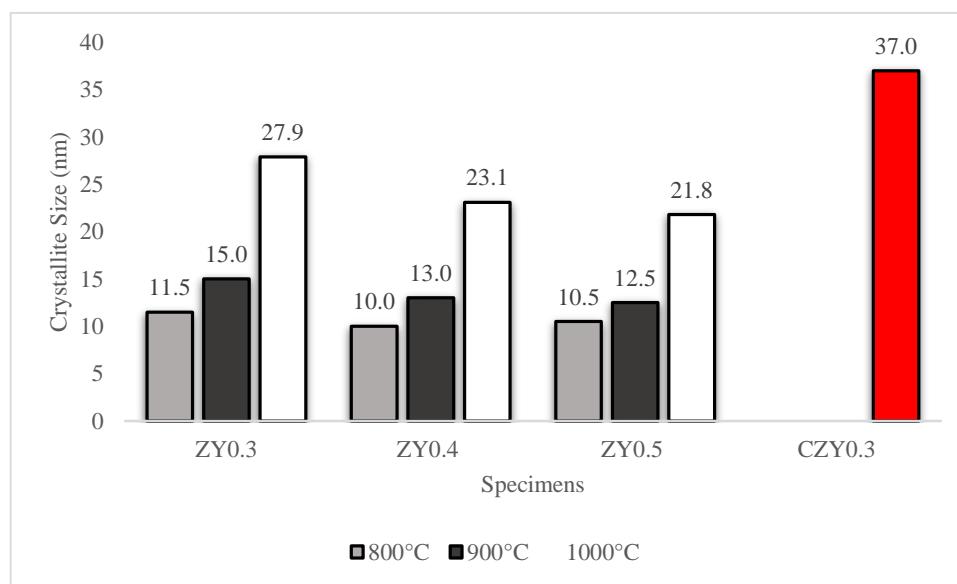
This same phase was found and reported by Grzebielucka et al (2010, when evaluated the characteristics of  $\text{ZrO}_2$  powders doped with  $\text{Y}_2\text{O}_3$  via Pechini Method using two distinct routes, with calcination temperature of 450 and 600°C for 2 and 24h, respectively. On the other hand, the authors note that the increase in calcination temperature and time, induce variations in intensity and width of peaks.

The problem to find the tetragonal phase (1 1 1) was previous reported for several researches. Stevens (1986) and Davar et al (2013) reported in their works this difficult to get the correct identification of the crystalline tetragonal phase, this fact occurs because the peaks overlap of the tetragonal to cubic and the similar lattice parameters “ $a$ ” using the simetric tetragonal structure (0.5094nm), as been the cubic structure of centered face (0.5124nm), are very similar. This trouble would minimized if the cubic structure of centered body, trying resemble with the Fluorite structure ( $\text{CaF}_2$ ), that comparatively make the easir and fast identification. Rashad et al (2008) and Kanad et al (2008) to check

this difficulty indicate the use of more techniques as Raman spectroscopy than a XRD complementary technique, due the crystallite size this structures are very small and as next values. This technique is sensible to polarization of oxygen ions to determine the crystal symmetry, widely quite used for polymorphic materials identification. In this study, for powders calcined at 1000 °C this behavior is more expressive than that in others calcination temperatures (800 and 900 °C), respectively.

These variations were assigned by difference in the crystallite sizes produced by different temperatures calcination employed. Note that the most significant changes occurred when the calcination temperature was increased from 800 °C to 1000 °C.

The crystallite sizes shown in Fig. 2.3 Were determined by XRD analysis, while the heights of the peaks shown in Fig. 2.2 were determined using Scherrer's equation (Scherrer, 1918). The zirconia crystallite size increased as calcination temperature increase. This behavior was observed to all specimens. The powders' crystallite size for specimens with 3% of Yttria ( $ZY_{0.3}$ ) plane (1 1 1) growth from 11.5 to 2.9 nm, i.e., 142,4% major, when the temperature was increased from 800 to 1000°C. For specimens with Yttria content (4% ( $ZY_{0.4}$ ) and 5% ( $ZY_{0.5}$ )), the crystallite sizes grew (10.0 to 23.1 nm and 10.5 to 21.8nm) in the same temperature range.



**Fig 2.3** Crystallite size of zirconia doped with Yttria in different contents ( $ZY_{0.3}$ ,  $ZY_{0.4}$  e  $ZY_{0.5}$ ) plane (1 1 1), obtaining by Pechini Method and commercial zirconia ( $CZY_{0.3}$ ).

The results indicate that the calcination at higher temperatures enables Y-doped zirconia to acquire larger crystallite sizes and higher crystallinity. The calcination temperature of 1000 °C was selected for further investigation of the particle properties. The effect of the complexation agents and metal ion concentration in the precursors, on the crystallization behavior of Yttrium doped Zirconia was also studied. This same behavior was reported by Davar et al (2013) and Grzebielucka et al (2010) they showed that the increase in calcination temperature can be increased the crystallite size of the zirconia powders. Thus, the increase in a calcination temperature promote a major atomic diffusion, increasing the structural packing that enhanced consequently the crystallite size.

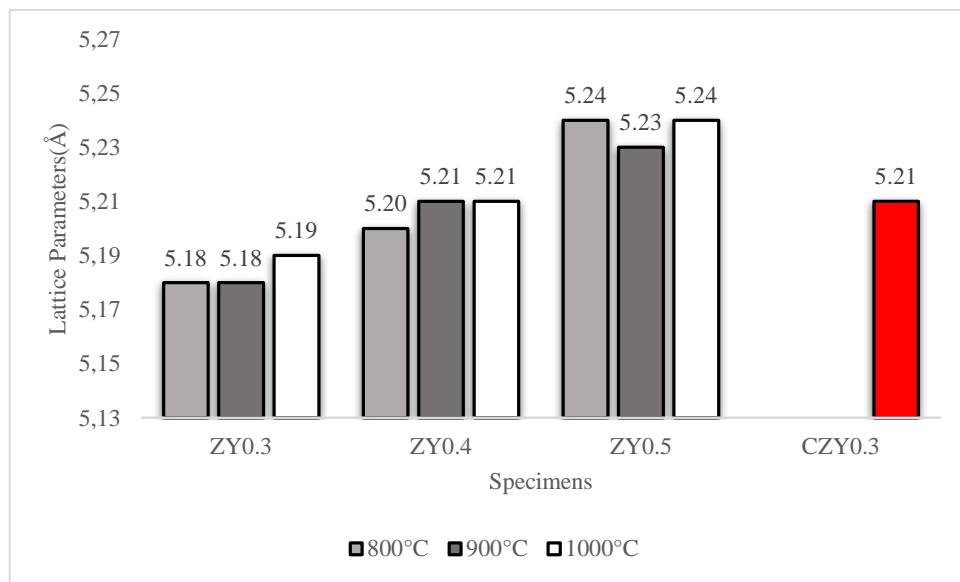
These results are in agreement as exhibit results in previous XRD (Fig 2.2). The dopant content is also an important factor to be evaluated. The increase of dopant content into crystal lattice promote the decrease in crystallite size for the same temperatures and distinct compositions. Chevalier et al (2009), reported that the  $\text{ZrO}_2$  compositions containing more than 8mol%  $\text{Y}_2\text{O}_3$  stabilize the cubic phase at room temperature, while compositions containing 2-3% stabilize the tetragonal phase, and compositions between these values generate a mixture of tetragonal and cubic phases.

However, in addition of the 3% of Yttria content, was used in this study the proportions (4 and 5 mol. %), these values are in a transition area to stabilization in 8%, i.e., the structure is not totally stabilized. Comparatively with commercial zirconia ( $\text{CZY}_{0,3}$ ) were found differences in crystallite size, i. e., for specimens with 3% of Yttria content assigned by CPM Method at 1000 °C the value was (27.9 nm), whereas for commercial zirconia this value was more higher (37.0 nm) when observed to all specimens before studieds. This result can be explain to according as achievement technique used.

The Fig. 2.4 show the calculated lattice parameters for specimens ( $\text{ZY}_{0,3}$ ,  $\text{ZY}_{0,4}$ ,  $\text{ZY}_{0,5}$  and  $\text{CZY}_{0,3}$ ), respectively (FullProf – Crystallographic Server). Is it possible to check that the lattice parameters no presents large variations with the increase of the calcination temperature for the same stoichiometry, as the case of specimen  $\text{ZY}_{0,3}$  (5.18 e 5.19 Å), an increase only 0.17%. The same behavior also can be seen for specimens  $\text{ZY}_{0,4}$  e  $\text{ZY}_{0,5}$ , that presents discrete difference to order 0.15%. The commercial zirconia no presents large differences in lattice parameters when compared with others specimens calcined at 1000°C. Thus, the difference in lattice parameters of the specimens synthesized and commercial are not significant.

On the other hand, the increase of Yttria content in network, promote some changes in lattice parameters as reported by Yamagata (2008), according to the author, in

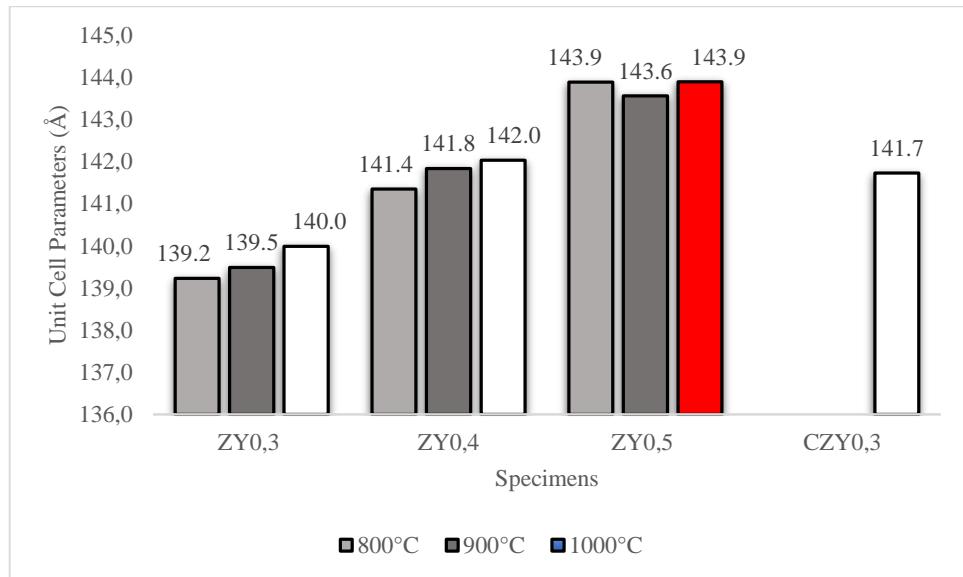
a structure model of the cubic zirconia stabilized with Yttria, while the oxygen and the vacancies occupy the anionic position in sub-lattice, the cations of zirconium and the dopants fill the structure of lattice of type cfc (centered cubic face), be the lattice parameter the half of cationic lattice cfc.



**Fig 2.4.** Lattice parameters of the zirconia doped with Yttria in different contents (ZY<sub>0,3</sub>, ZY<sub>0,4</sub> e ZY<sub>0,5</sub>) by CPM and commercial zirconia (CZY<sub>0,3</sub>).

The Fig. 2.5 show the unit cell parameters for specimens (ZY<sub>0,3</sub>, ZY<sub>0,4</sub> e ZY<sub>0,5</sub>) with calcination temperature (800 °C, 900 °C e 1000 °C) and commercial zirconia (CZY<sub>0,3</sub>), respectively. For the same composition and distinct calcination temperatures, the unit cell volume was quite similar (139.2 to 140.0 Å - ZY<sub>0,3</sub>; 141.4 to 142.0 Å - ZY<sub>0,4</sub>; 143.6 to 143.9 Å - ZY<sub>0,5</sub>), including the zirconia commercial (141.7 Å - CZY<sub>0,3</sub>).

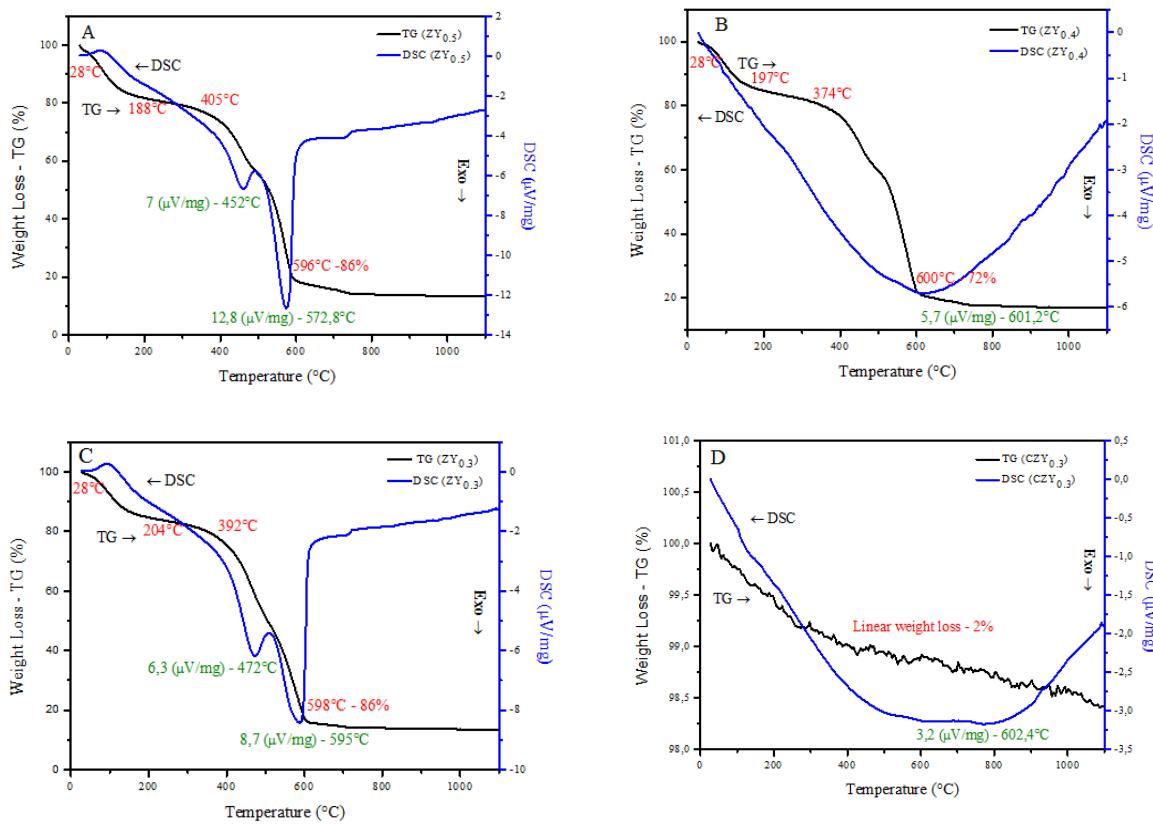
However, with the increase of the Yttria content, it is possible to see changes in unit cell volume, this behavior can be explained, by decrease in tetragonal phase (metastable) with increase in amount dopant. Thereat, the zirconia structure tends to change for cubic phase, this phase presents the major values of unit cell volume (Silva et al, 2010). In this case, emphasis will be placed on the minor stabilizing contribution of the dopant cations. The distribution of dopant cations and anions vacancies, may assume local short-range configurations that give rise to different degrees of relaxation of the anion packing around the average host cation, presents direct influence of unit cell volume (Jessica et al, 2008; Durand et al, 2012; Casellas et al, 2001).



**Fig. 2.5** Unit cell parameters of the zirconia doped with Yttria in different contents (ZY<sub>0,3</sub>, ZY<sub>0,4</sub> e ZY<sub>0,5</sub>) obtaining by Pechini Method and commercial zirconia (CZY<sub>0,3</sub>).

The thermal behavior of the doped Yttria-Zirconia by (CPM) and commercial zirconia at 1100 °C, was performed. The pyrolysed material at 350 °C/4h, was analyzed by thermoanalyses (TGA/DTA), present informations related to decomposition and weight loss in different stages.

The decomposition progress is in several steps and is based on a thermally induced anionic redox reaction. The Fig. 2.6 shows the thermoanalysis (DTA/TGA) and mass spectrometry analyses for calcined specimens at 1000 °C (ZY<sub>0,3</sub> - A, ZY<sub>0,4</sub> - B, ZY<sub>0,5</sub> - C and CZY – D), respectively. Fig. (2.6A) shows that the initial and second weight loss occurs between 28 to 204 °C and 392 to 598 °C (weight loss of 85%), respectively. Fig (2.6B) shows the initial weight loss between 28 to 197°C and the second weight loss (374 to 600°C), with weight loss of 72%. The Fig. (2.6C) shows the initial weight loss (28 to 188°C) and the second weight loss is observed between 405 to 596°C and the percent of weight loss of around 86%.



**Fig. 2.6** TGA/DTA curves of specimens with varied of Yttria content in Zirconia (A, B, C) and commercial zirconia (D).

Fig. (2.6D) show the linear weight loss with increase of temperature, around 2%. Comparatively with others specimens (A, B and C), this result can be explained due the different method of manufacturing employed, in commercial zirconia was used the high energy ball-milling. Instead, the no existence of the other peaks until the temperature of 1100°C, these materials can be featured as thermally stable. The transformation from amorphous powder into a crystallized homogeneous oxide phase corresponds to an endothermic and two exothermic peaks in the DTA curve for specimens (A, B and C), respectively.

The first one is related to the evaporation of the excess volatile material, in special the water evaporation, also by citric acid dissolution in water during the achievement process metallic citrates, besides the existence of adsorbed gases of compound. The second and third peaks corresponds to the energy release (CO<sub>2</sub> and NO) during combustion reaction of organic compounds, nitrates decomposition and material crystallization. The presence of CO, CO<sub>2</sub>, H<sub>2</sub>, N and N<sub>2</sub> compounds in resin obtained by CPM, can lead a volatilization with a large weight loss.

The TGA curves show mass change of a sample as a function of temperature or time in a temperature controlled environment and atmosphere. The specimen with 3% of Yttria dopant ( $ZY_{0.3}$  – A), present the loss energy in 6,3 and 8,7 ( $\mu V/mg$ ) at 440.5 and 595 °C, respectively. In specimen ( $ZY_{0.4}$  - B) the exothermic peak obtained an loss energy of 5.7 ( $\mu V/mg$ ) at 601.2 °C, this temperature refers to the energy release during the organic material combustion. The specimen with 5% of Yttria dopant ( $ZY_{0.5}$  – C) presented exothermic peaks of 7 e 12.8 ( $\mu V/mg$ ) at 452°C and 572.8°C, assigned by organic material combustion (energy release) and oxidation reaction of  $Zr^{4+}$  ions that remain in fluorite structure. In commercial zirconia specimen ( $CZY_{0.3}$  – D) occurs the short energy loss 3.2 ( $\mu V/mg$ ) at 610.4°C.

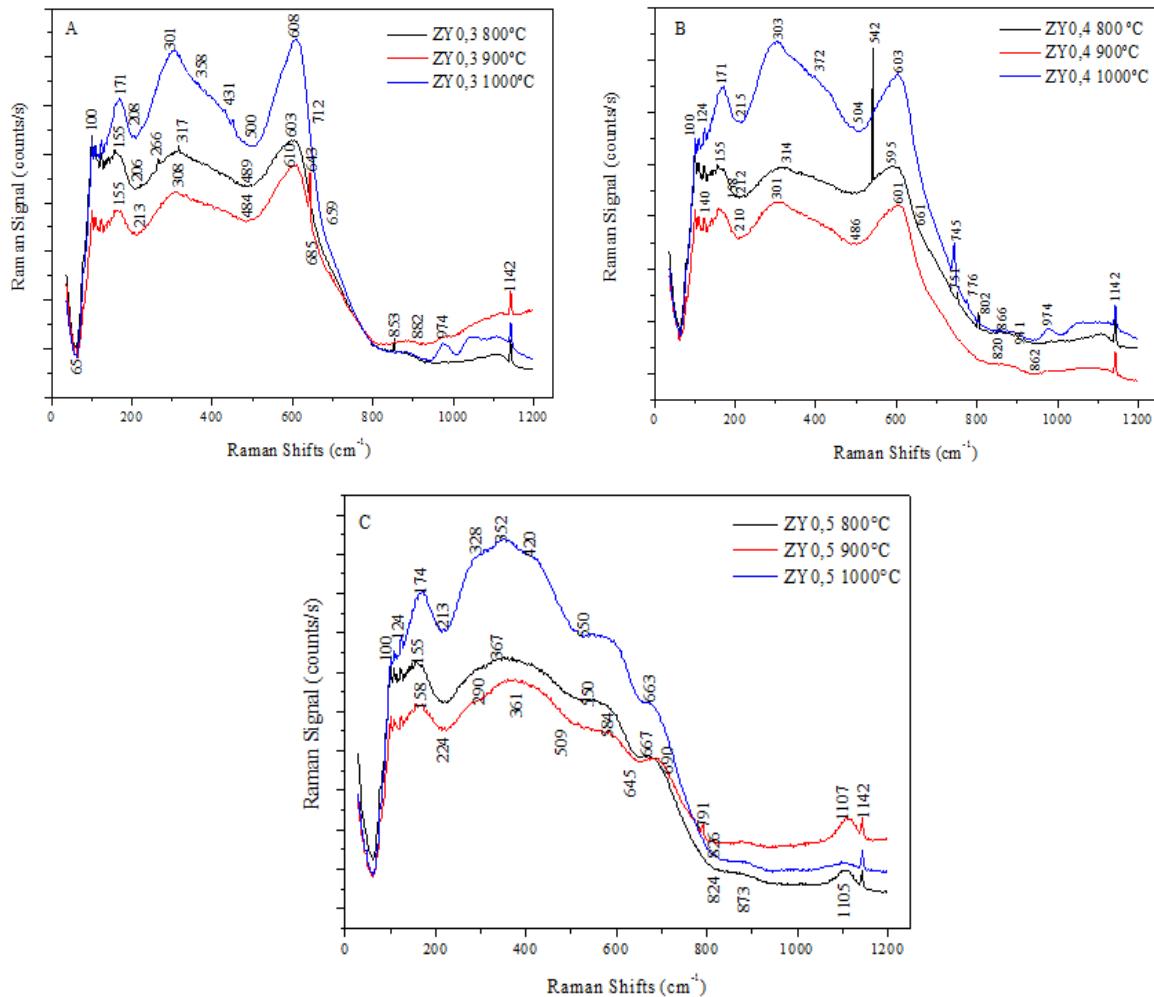
The Raman spectroscopy determine the phases present is to observe the vibrations of the atoms in the sample structure, can be used in solutions and solids as well as characterization of molecular or crystalline structure, collects information relating to the frequencies at which chemical bonds vibrate (Brundle et al, 1992). The broadening of the Raman peaks is usually a result of structural disorder within the sample from amorphous regions, doping, defects, or small particles sizes. The Raman spectroscopy is very flexible and has been used by researchers to characterize the monoclinic-to-tetragonal and tetragonal-to-cubic phase transformations that occur in zirconia materials as a result of a change in temperature (Siu et al, 1999), the addition of dopants (Fernandez-Lopes et al 2001; Li and Li, 2002) or an applied stress (Li et al, 2003).

The Fig. 2.7 shown the Micro-Raman spectra for specimens. Were compared the spectra with similar Yttria content in zirconia powders and varied calcinations temperature (800, 900 and 1000 °C). It is possible to see that independent of calcination temperature employed, all specimens presents the monoclinic and tetragonal phases and the mixture of both. The Fig. 2.7 (A) Raman spectra showed the  $ZY_{0.3}$  at 800, 900 and 1000 °C, respectively.

According to these spectras, in specimens calcined at 1000 °C the peaks of  $100\text{ cm}^{-1}$  indicate the presence of monoclinic phase (m-phase),  $171\text{ cm}^{-1}$  monoclinic phase (m-phase),  $301\text{ cm}^{-1}$  the mixture of tetragonal and monoclinic phases and  $431\text{-}608\text{ cm}^{-1}$  tetragonal phase. When the calcination temperature was reduced at 900 and 800 °C, the characteristic of m-phase practically no exist and the peaks located at 155, 266, 317 and  $608\text{ cm}^{-1}$  confirms t-phase of zirconia successfully obtained.

The Fig. 2.7(B) show the spectra of  $ZY_{0.4}$  at 800, 900 and 1000 °C, respectively. Can be seen in this spectra the presence of monoclinic phase at  $171\text{ cm}^{-1}$  tetragonal and

monoclinic phase at  $303\text{ cm}^{-1}$ , monoclinic phase at  $372\text{ cm}^{-1}$  and tetragonal phase at  $603\text{ cm}^{-1}$ . Upon reducing the calcination temperature from 900 and 800 °C this peaks are 100  $\text{cm}^{-1}$  monoclinic phase, t-phase 140 and 155  $\text{cm}^{-1}$ , monoclinic phase at 800 °C - 222  $\text{cm}^{-1}$ , mixture of phase tm at 301 and 314  $\text{cm}^{-1}$ , mixture of cubic and tetragonal phase at 542  $\text{cm}^{-1}$  and tetragonal phase at 601 and 595, respectively.



**Fig. 2.7** Raman spectrometry of Yttria doped zirconia in different contents and calcination temperature.

Fig. 2.7(C) show the behavior of peaks for specimens with 5% of Yttria content in zirconia calcined at different temperatures. For calcination temperature at 1000 °C the monoclinic phase can be see with the peaks 100, 171 and 352  $\text{cm}^{-1}$ , tetragonal phase 323 and 420  $\text{cm}^{-1}$  and the mixture tm at 550  $\text{cm}^{-1}$ . In temperatures of the 900 and 800 °C the wavenumbers of the peaks are monoclinic phase 100 and 361  $\text{cm}^{-1}$  for 900 °C and 367  $\text{cm}^{-1}$  for 800 °C, tetragonal phase at 290, 584 and 645  $\text{cm}^{-1}$  – 900 °C and 155  $\text{cm}^{-1}$  – 800 °C and lastly the mixture of monoclinic and tetragonal phases at 550 and 667  $\text{cm}^{-1}$  - 800 °C.

The changes in zirconia bond angles and lengths allow to identify the phase transformations (monoclinic, tetragonal and cubic), this behavior is evaluate by various authors (Casellas et al, 2001; Bouvier et al 2001; Ishigame et al, 1977; Ramos et al, 2013), observed that the main broad bands for zirconia were approximately 260, 464, and 642 cm<sup>-1</sup>, this values are characteristics of the tetragonal and cubic phases (Casellas et al, 2001).

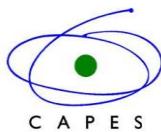
In this study, the difference of calcination temperature and chemical stabilizers (Casellas et al, 2001; Bouvier et al 2001; Ishigame et al, 1977; Ramos et al, 2013) and crystal sizes probably caused few spectral variations at the tetragonal and cubic phases. However, unlike indicated for standard letter (X'pert 77-2113), the phase obtained with sucess for all calcination temperature, was the tetragonal phase and no cubic phase as reported before. This result also was observed by Davar et al (Davar et al, 2013) where decrease the calcination temperatures was possible to obtain the tetragonal phase. Comparatively as X-Ray diffraction the Raman spectroscopy indentify the phases from the vibrational modes of atomic bonds with laser radiation (visible, IR, UV) while the XRD detect phases in quantities > 1-2 wt% and particle sizes < 100nm. Thus, the Raman spectroscopy is considered a complementary technique to indentify the phases presents of the materials and more indicate to identify the polymorphic phases existing in zirconia powders.

#### 4. Conclusions

The CPM is a good technique to produce monophasic zirconia with different Yttria contents. Crystallographic parameters of the synthesized specimens no presents large variations compared as zirconia commercial. Calcination temperature was a significative factor to changes the peaks intensity and consequently the cristallinity of the specimens. Specimens synthesized presents the large weight loss when compared as commercial zirconia, this fact is dependent of the type of manufacturer technique used.

## Acknowledgments

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## **CHAPTER III**

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### **Strenghtening and Toughening of dental porcelain by the inclusion of an yttria-stabilized zirconia reinforcing phase**

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#### **Abstract**

The aim of this work was to evaluate the microstructural and mechanical performance of dental porcelain composites reinforced and toughened by 20vol.% tetragonal zirconia (3Y-TZP). Two Types of particles were tested: yttria-stabilized zirconia ( $ZrO_2$ -3%  $Y_2O_3$ ) agglomerates and pre-sintered yttria-satabilized zirconia ( $ZrO_2$ 3%  $Y_2O_3$ ) particles and processed by hot pressing technique at 970°C. The composites were analyzed by the means Scanning Electron Microscopy (SEM), Energy Dispersion Spectroscopy (EDS) and XRD Diffraction (XRD). The mechanical properties were obtained by the transverse rupture strength test. The best mechanical results were displayed by the porcelain reinforced with the pre-sintered  $ZrO_2$ -3%  $Y_2O_3$  particles (ZP).

**Keywords**—Composite, dental restoration, porcelain, strengthening, toughening, wear, zirconia.

## 1. Introduction

The use of ceramics in dentistry is nowadays the mainstream in aesthetical restorative dentistry. Zirconia is in the forefront of this trend due to its biocompatibility, aesthetics (Jing et al, 2014) corrosion resistance (Chevalier et al, 2009) and good mechanical properties relative to alternative materials. Zirconia-based restorations comprise a strong and thought zirconia substructure that is veneered with a weaker compatible porcelain that is used to mimic the color of real teeth and eventually to reduce the wear of the dental restoration with the opposite teeth.

Zirconia is a polymorphic ceramic with different crystal structure at different temperatures, but keeping the same chemistry. Zirconia can be found in three crystalline forms: monolithic; tetragonal and cubic. Pure zirconia is stable in monoclinic phase at room temperature. At 1173°C it undergoes a phase transformation from monoclinic to tetragonal and then to cubic at 2370°C. Above 2690°C zirconia melts.

These transformations are reversible upon cooling with the tetragonal to monoclinic (t-m) transformation imparting compressive stresses to the material due to the volume expansion of 4-5% that occurs with the transformation. It is possible to fully or partially stabilize zirconia in its tetragonal or cubic form at room temperature by alloying it with other cubic oxides termed as “stabilizers”. Calcia, magnesia, ceria, alumina or yttria are used for that end. Zirconia is said to be partially stabilized (Partially Stabilized Zirconia – PSZ) when a multiphase form coexists in the material: cubic as the major phase and monoclinic and tetragonal zirconia precipitates, as the minor phase.

To date, the best properties are exhibited by zirconia stabilized with  $\text{Y}_2\text{O}_3$  (yttria), where the whole material is constituted by transformable t-zirconia grains and called Tetragonal Zirconia Polycrystals (TZP). The addition of 2-3 mol% yttrium oxide ( $\text{Y}_2\text{O}_3$ ) as stabilizing agent results in a fully tetragonal fine-grained zirconia ceramic material with 100% small metastable tetragonal grains (Y-TZP). This type of zirconia has been extensively used in dental frameworks for all-ceramic restorations. Partially stabilized zirconia displays a toughening mechanism that uses the t-m transformation to arrest the crack propagation, and is therefore termed transformation toughening. When a crack arises in zirconia, the stress field generated at the crack tip causes a local phase transformation from the metastable tetragonal phase to monoclinic phase. This transformation is accompanied to a volume increase of the crystals, constrained by

surrounding ones, and a compressive stress field is generated at the crack surfaces near the crack tip that tend to pinch the crack shut, thereby hindering its propagation.

Dental porcelains, as well as other several glass-ceramics used in biomedical applications lack in mechanical properties that allow them to be employed in load-bearing applications. Therefore, some authors addressed their efforts to toughen these materials by adding a second high-strength biocompatible phase (Ferraris et al, 1996; Verné et al, 1998; Verné et al, 1999; Verné et al, 2000, Kasuga et al, 1992, Kasuga et al, 1998, Fusayama et al, 1963).

In this work, two types of zirconia particles were used as reinforcing phase in the pressure assisted (hot pressed) sintered composites: yttria-stabilized zirconia ( $\text{ZrO}_2$ –3%  $\text{Y}_2\text{O}_3$ ) agglomerates and pre-sintered yttria-stabilized zirconia ( $\text{ZrO}_2$ –3%  $\text{Y}_2\text{O}_3$ ) particles. The influence of these two types of reinforcing phases in terms of mechanical and wear properties was investigated. Results were compared with monolithic porcelain obtained under the same processing conditions.

## 2. Materials and Methods

The zirconia ( $\text{ZrO}_2$ –3%  $\text{Y}_2\text{O}_3$ ) agglomerates (named as ZA (A) from now on) were used as received by the manufacturer (Innovnano, Portugal) and blended with the porcelain powders (Vita VM9, Vita) in a rotation machine during 24h. The zirconia content in all mixtures was 20%, vol.%. Porcelain feldspathic powders with 0% of volume content are named Z0 (B) from now on.

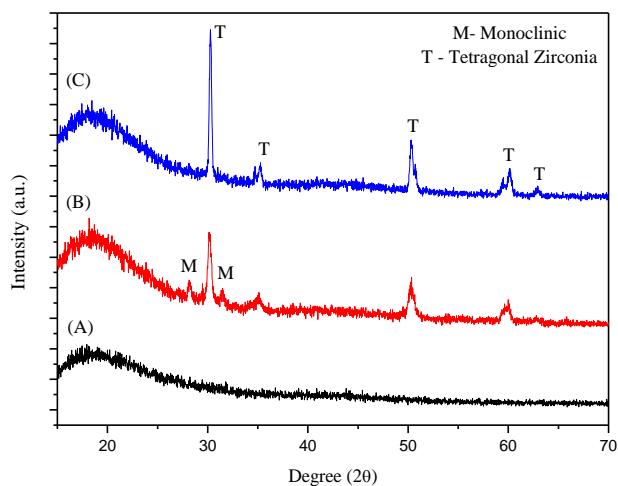
The pre-sintered zirconia powders (named ZP (C) from now on) were obtained out of the sintered agglomerates provided by the supplier. Zirconia agglomerates were sintered in a furnace (ZirconZhan) at 1500°C for 2h. Afterwards, powder mixtures (pure porcelain feldspathic and zirconia) were ball milled to reduce agglomeration and to enhance mixing, respectively.

Specimens were heat pressed in vacuum, at 970°C for two minutes and pressure (7MPa). The mechanical properties were assessed by the means of a 3-point bending flexural test. The crosshead speed was 0.5 mm/s and the load cell used had 25kN of capacity. The microstructure and fractured surfaces were observed by XRD and SEM, respectively.

### 3. Results

#### 3.1 Microstructural Analysis

The X-ray diffraction patterns for standard and glancing angles are show in Fig. 3.1. The Figure presents the upper scans of the feldspathic porcelain – Z0 (A), feldspathic porcelain reinforced composites with zirconia agglomerates - ZA (B) and feldspathic porcelain reinforced composites with zirconia particles – ZP (C) prepared by mixing and hot pressing technique. Tetragonal peaks at approximate ( $30.2^\circ 2\theta$   $35.1^\circ 2\theta$ ,  $50^\circ 2\theta$ ) were indentified for specimens (B) and (C). Is it possible to see the presence of an additional monoclinic peak at approximately  $28.2^\circ 2\theta$   $\square\square\square$   $32^\circ 2\theta$  was detected for specimen (B). In specimens tested (B) and (C) at glancing and standard angles showed an increase in tetragonal phase as the sintering temperature increased.

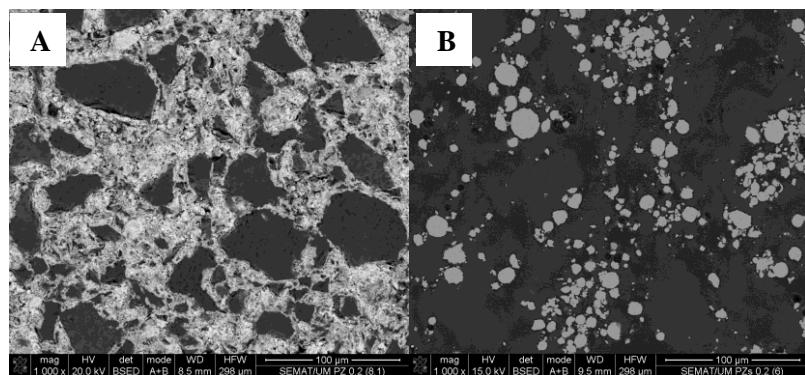


**Fig. 3.1** Diffractogram of the (A) Feldspathic porcelain – Z0, (B) Feldspathic porcelain reinforced composites with zirconia agglomerates - ZA and (C) feldspathic porcelain reinforced composites with zirconia particles - ZP.

The effect of particles and agglomerates in feldspathic porcelain matrix compared as feldspathic porcelain was measured. The presence of tetragonal phase in specimens (B) and (C) is resulted of the insertion of (3Y-TZP) in porcelain matrix. The intensity of the peaks (C) is most expressive when compared as (B) due the powders sintered presents a larger crystalline organization at  $1500^\circ\text{C}/2\text{h}$  (sintering temperature) increased the

tetragonal phase in relation the others specimens. The feldspathic porcelain (A) presents amorphous characteristics.

Fig. 3.2 shown the micrographs of the zirconia reinforced feldspathic porcelain composites, zirconia agglomerates (A) and zirconia particles (B). The two microstructures produced are significantly different from each other, which might indicate different sintering behaviors.

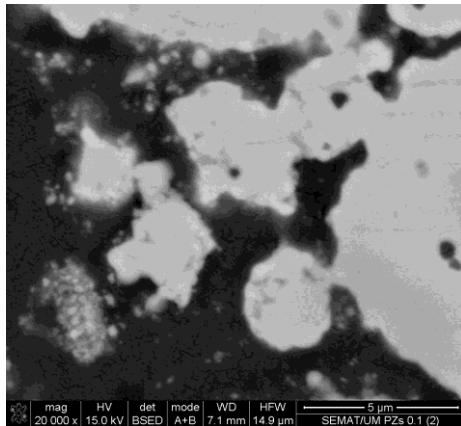


**Fig. 3.2** Micrographs of the feldspathic porcelain composites reinforced zirconia agglomerates (**A** - ZA) and zirconia particles (**B** - ZP). Zirconia appears as white phase and porcelain as dark phase.

In specimens with zirconia agglomerates (ZA) it is not visible the zirconia agglomerates, suggesting that they were destroyed during the mixing procedure. The white phase in Fig. 3.2 is the pulverized zirconia powder that covered the feldspathic porcelain powders and negatively impacted the sintering of the composite.

On the other hand, in specimens with zirconia particles (ZP) it is possible to see round zirconia particles spread through the feldspathic porcelain matrix. Few pores can be detected within the porcelain matrix of feldspathic porcelain/zirconia-porcelain samples and they are preferentially located at the vicinities of the ZPs rather than in the porcelain matrix.

Fig. 3.3 shown the interface between the reinforcing zirconia particles phase and feldspathic porcelain matrix. The micrographs of the fractured surfaces zirconia reinforced feldspathic porcelain composites, (feldspathic porcelain, zirconia agglomerates and zirconia particles), respectively.

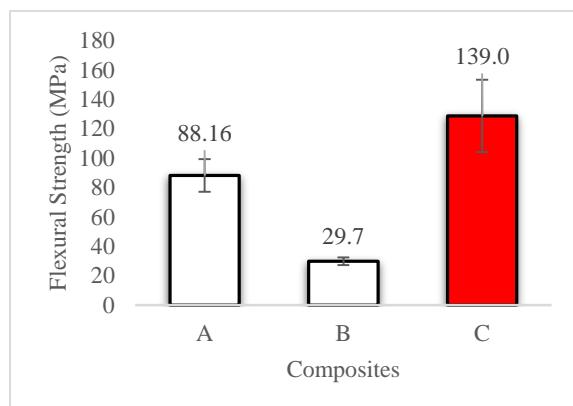


**Fig. 3.3** Detail of the interface between the zirconia particle ZP (white phase) and the feldspathic porcelain (dark phase).

In Fig. 3.3, the detail of the interface between the reinforcing Zirconia particles (ZP) phase and the matrix is presented. It shows a good bonding between the zirconia particles (ZP) and the matrix and a complete infiltration of the matrix inside the topological details of the ZPs.

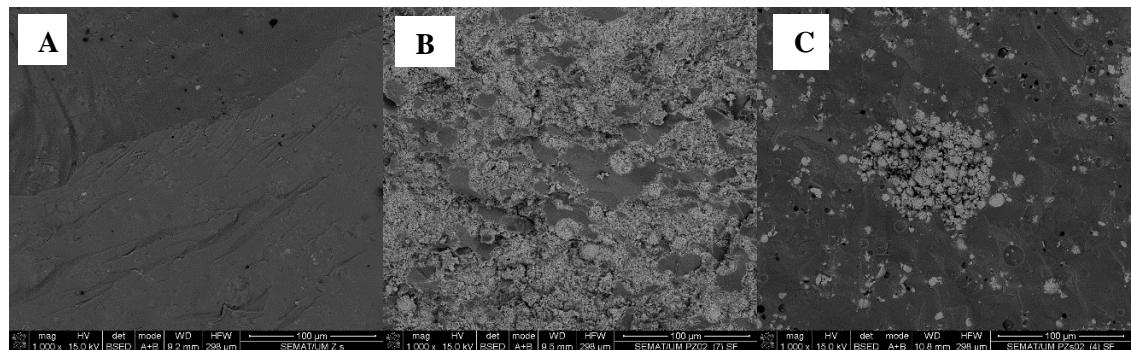
### 3.2 Mechanical Tests

The Fig. 3.4 shows the flexural strength of the composites ZA (B) and ZP (C) when compared to the feldspathic porcelain (Z0). The zirconia agglomerates (ZA) showed to produce a detrimental effect on the strength of the composites relative to pure porcelain. On the other hand, the pre-sintered zirconia particles (ZP) showed to improve significantly the flexural strength of the composite relative to pure feldspathic porcelain (Z0).



**Fig. 3.4** Flexural strength of the (A) feldspathic porcelain, (B) feldspathic porcelain reinforced composites with zirconia agglomerates and (C) zirconia particles.

The fractured surfaces zirconia reinforced porcelain composites, (feldspathic porcelain, zirconia agglomerates and zirconia particles), respectively are shown in Fig. 3.5.



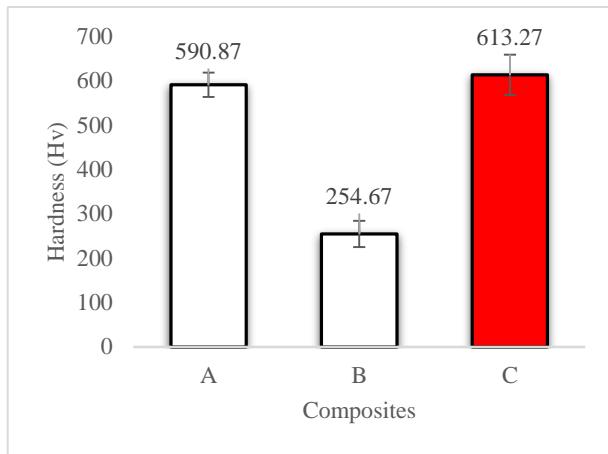
**Fig. 3.5** Micrographs of the polished fractured surfaces of three composites. (A) Feldspathic porcelain, (B) feldspathic porcelain reinforced composites with Zirconia particles and (C) feldspathic porcelain reinforced composites with Zirconia agglomerates.

In dentistry, the most common complication observed in zirconia-based restorations was fracture of the veneering porcelain, manifesting clinically as chipping fractures of the veneering ceramic with or without exposing the underlying Y-TZP substructure (Al-Amleb et al, 2010).

The fracture mode is directly related to presence and type of zirconia reinforcement in glass ceramic matrix. The Fig 3.5 (A) Show the characteristic brittle fracture in feldspathic porcelain (Z0). The Fig 3.5 (B) present the fracture surface of the feldspathic porcelain reinforced as zirconia agglomerates, the presence of the agglomerates decrease the mechanical properties of these composites due the lower bond between zirconia agglomerates and porcelain powders.

Beside, the processing temperature (970°C) it is not enough to consolidate the microstructure agglomerates. The feldspathic porcelain reinforced as zirconia particles (Fig. 3.5 (C), present the superior mechanical properties than compared as (A) and (B) specimens. The pre-sintered particles Fig 3.5 (C) act as slow crack and consequently increase the mechanical properties of these composites.

The hardness behavior to feldspathic porcelain (A), feldspathic porcelain reinforced with zirconia agglomerates (B) and particles (C) can be show in Fig. 3.6.



**Fig. 3.6** Vickers Hardness of the (A) Feldspathic porcelain, (B) Feldspathic porcelain reinforced composites with zirconia agglomerates and (C) zirconia particles.

The results presented in Fig. 3.4 and 3.6, show clear differences between composite in flexural strength and hardness to according as type of reinforcing phase used. Samples with 20% reinforcing phase zirconia agglomerates, showed lower flexural strength and hardness (29,7MPa and 254,67Hv), when compared as monolithic porcelain (0% zirconia) and composites with 20% zirconia particles, respectively.

#### 4. Discussion

The microstructural and mechanical properties of the composites were strongly influenced by the type of reinforcing phase that was used in each composite: zirconia agglomerates (ZA) and zirconia particles (ZP). The increase of the tetragonal phase as previously reported, is related to the previous heat treatment of the zirconia agglomerates at 1500 °C/2h. The low strength observed in the (ZA) composites was due to the destruction of the zirconia agglomerates during the powders mixing process. This produced a fragmentation of the powders in micrometric and nanometric powders that covered the powders of porcelain and did not allowed the fused porcelain powders to bond with each other. Most of the feldspathic porcelain powders were covered by fine zirconia particles that sinters at 1500°C and not at 970°C as happens with porcelain. The

work of (Verné et al 2003) suggests that if the zirconia agglomerates were maintained in the powder mixture without being destroyed (switch the ball mill of powders by steering suspension of the mixture in alcohol until complete evaporation) the mechanical strength could be even increased. The mechanism was explained by the infiltration of the porcelain phase into the zirconia agglomerates, leading to a partial spreading of each particle into agglomerates of small zirconia grains (about 1 µm size).

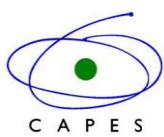
On the other hand, the improvement in the flexural strength of the composite (ZP) relative to pure porcelain is explained by the action of the uniformly distributed dense zirconia particles (pre-sintered agglomerates). The zirconia particles act as a second phase that is more rigid than the porcelain matrix, allowing the load transfer reinforcing mechanism to occur from matrix to the reinforcing phase. Besides the improvement noticed in flexural strength of the (ZP) it is also expected an improvement in the toughness behavior relative to pure feldspathic porcelain (Verné et al 2003). The toughening mechanism is based on the crack deflection around the zirconia particles.

## 5. Conclusion

Two types of dental porcelain based composites reinforced by zirconia agglomerates (ZA) and zirconia particles (ZP) were produced by pressure assisted sintering. The best mechanical properties were found for (ZP) specimens due to a good dispersion and good bonding between the reinforcing zirconia phase and the feldspathic porcelain matrix. The pulverization of the zirconia micro/nano particles during the blending process of the porcelain powders-zirconia agglomerates showed to impart problems to the sintering and densification of (ZA) composites, reducing dramatically the strength of the composite.

## Acknowledgment

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## **CHAPTER IV**

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### **On the mechanical properties and microstructure of zirconia-reinforced porcelain for prosthetic dentistry**

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#### **Abstract**

**Objective:** The aim of this study was to produce and to evaluate the mechanical properties of a dental feldspathic porcelain reinforced by zirconia particles.

**Methods:** The specimens were prepared by incorporating different volume fractions (10, 20, 30, 40 or 50%) of zirconia particles (3Y-TZP) in a feldspathic porcelain matrix. The mixtures were hot pressed in vacuum at 970°C for 2 min. Flexural strength of the composites were measured using a three-point-bending test. Micro-Hardness, Young's modulus and fracture toughness were also measured for all the composites. The microstructure and fracture surfaces were characterized by (FEG-SEM). Chemical analyses were performed by Energy Dispersive Spectroscopy (EDS) and X-Ray Diffraction (XRD).

**Results:** The highest flexural strength ( $218 \pm 24$  MPa) and fracture toughness ( $2.1 \pm 0.9$  MPa m $^{1/2}$ ) values were recorded for composites containing 30% zirconia particles. That corresponded to improvement in mechanical properties of about 2 times relative to those registered for feldspar-based porcelain.

**Conclusions:** The addition of zirconia particles to porcelain improved significantly the mechanical properties of the base material. Zirconia-reinforced porcelain can constitute a promising alternative to conventional feldspar-based porcelains to produce prosthetic restorations, mainly for posterior teeth where high strength and toughness are demanded.

**Keywords:** porcelain, zirconia, heat pressing, composites, mechanical properties.

## **1. Introduction**

All-ceramic restorations have been increasingly used in prosthetic dentistry since they positively address the aesthetic and biocompatibility. Nowadays, restorations based on zirconia substructures veneered by aesthetical porcelain are the most widely used in single and multi-unit prostheses.

Zirconia is a polymorphic ceramic with different crystalline structures at different temperatures, but keeping the same chemistry. Zirconia can be found in three crystalline forms: monolithic (m-t; 1173°C); tetragonal (t-c; 2370°C) and cubic (c-melting temperature; 2690°C). Such transformations are reversible upon cooling from tetragonal to monoclinic (t-m) transformation resulting in compressive stresses to the material due to the occurrence of 4-5% volume expansion. Thus, calcia (CaO), magnesia (MgO), ceria ( $\text{CeO}_2$ ), alumina ( $\text{Al}_2\text{O}_3$ ) or yttria ( $\text{Y}_2\text{O}_3$ ) are used as stabilizers of the tetragonal phase. Yttria-stabilized tetragonal zirconia policristal (Y-TZP) has been used to produce dental prosthetic infrastructures, due to its excellent mechanical properties traduced in high flexural strength (up to 900-1200 MPa) and high fracture toughness ( $5.9-10 \text{ MPa m}^{1/2}$ ) (Sevilla et al 2010; Kosmac et al 1999; Piconi and Maccauro 1999). The addition of 2-3 mol%  $\text{Y}_2\text{O}_3$  results in a fully tetragonal fine-grained zirconia ceramic with 100% small metastable tetragonal grains (Y-TZP).

Despite the aesthetical and biocompatibility improvements over metal-ceramic systems, the failure rate of all-ceramic restorations by chipping or delamination of the veneering porcelain are still high (Donovan 2009; Sailer et al, 2009; Tan et al, 2004 Larson et al 2013; Aboushileb et al 2009; Bonfante et al 2009; Liu et al, 2015). Both systems present similar fracture mechanisms that rely either in edge chipping or interfacial fracture (delamination) of the veneering porcelain (Sailer et al, 2009; Tan et al, 2004 Larson et al 2013; Aboushileb et al 2009; Bonfante et al 2009; Liu et al, 2015).

Nevertheless, in vitro and in-vivo fatigue studies have shown that failure of dental prostheses implies crack propagation towards the interface (Bonfante et al 2009; Baldassari et al 2011; Coelho et a, 2009). The long-term success of the prosthesis is achieved if the crack formation could be eliminated or delayed. The strengthening of ceramics have been studied regarding several mechanisms such as: introduction of compressive residual stress fields at ceramic layers, infiltration of glasses with a lower coefficient of thermal expansion, chemical treatments, tailoring graded structures and introduction of inorganic particles (Green et al 1999; Vhantikul et al 1979; Green et al

1983; Balakishnan et al 2007; Chu et al 2007; Zhang et al 2012; Suresh 2001; Chai et al 2014).

Huang et al. (Huang et al, 2014), studied the microstructure and mechanical properties of zirconia-toughened lithium disilicate glass-ceramic composites containing different zirconia content (0-30 wt.%) by hot pressing technique at 800°C. The mechanical properties of the composite containing 15%wt. zirconia increased up to 340 MPa and 3.5 MPa m<sup>1/2</sup> relative to those of zirconia-free glass-ceramic. Verné et al. (Verné et al 2003) also showed the improvement of the flexural strength and fracture toughness of a glass-ceramic when reinforced with zirconia particles. In previous studies, we have shown the influence of metallic particles in the mechanical properties of dental porcelain (Henriques et al 2014).

The present study evaluated the influence of Y-TZP particles as a reinforcing phase on feldspathic porcelains. It was hypothesized that the presence of zirconia particles dispersed thought out the porcelain matrix can improve strength and toughness of the feldspathic porcelain. Depending on the prosthesis location, zirconia-reinforced porcelain can fully or partially replace the feldspathic porcelain. Hence, full replacement can occur in posterior restorations where higher loads are present and lower aesthetic is demanded. Partial replacements by using interlayer between zirconia substructure and veneering feldspathic porcelain, can be used in anterior teeth in order to meet the esthetic requirements.

## 2. Materials and Methods

### 2.1. Base materials

Dental porcelain and Y-TZP powders used in this study are shown in Table 4.1.

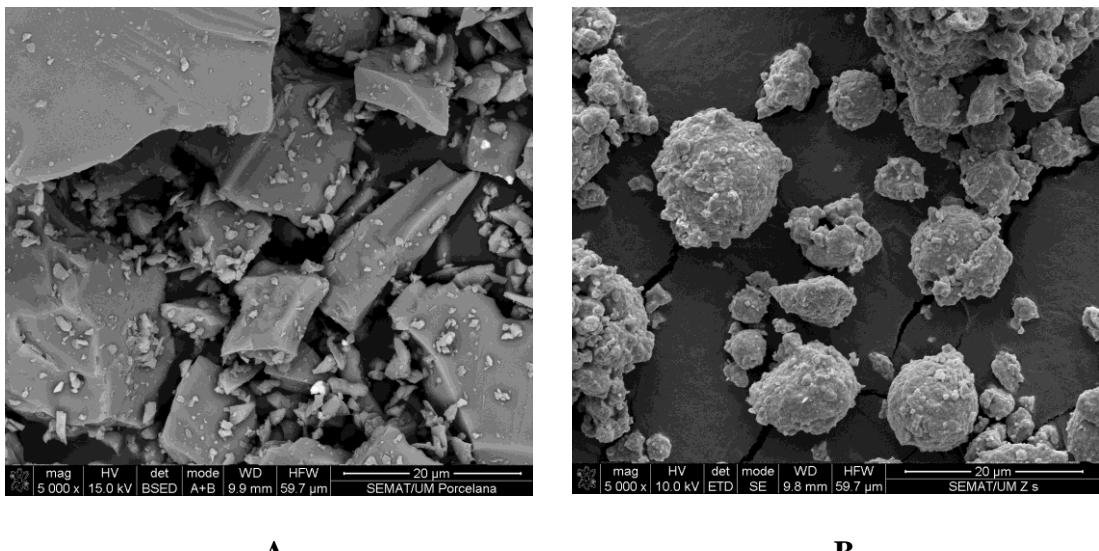
**Table 4.1.** Chemical composition, material and manufacturer of porcelain and Y-TZP used in this study.

Manufacturer/Brand	Chemical composition	Material	Batch
VITA VM9 Base	SiO <sub>2</sub> (60-64%), Al <sub>2</sub> O <sub>3</sub> (13-15%), K <sub>2</sub> O (7-10%), Na <sub>2</sub> O (4-6%), TiO <sub>2</sub> (<0,5%), CeO <sub>2</sub> (<0.5%), ZrO <sub>2</sub> (0-1%), CaO (1-2%), B <sub>2</sub> O <sub>3</sub> (3-5%), BaO (1-3%), SnO <sub>2</sub> (<0,5%), Mg, Fe and P oxides (<0,1%).	Feldspar-based porcelain	Vita Zahnfabrik, Bad Säckingen, Germany
Dentim –V9 Shade 3M2 (Lot n. 44670)			
3YSZGSB – Zirconia (Lot n. 1301PA046)	ZrO <sub>2</sub> + HfO <sub>2</sub> + Y <sub>2</sub> O <sub>3</sub> + Al <sub>2</sub> O <sub>3</sub> (99,9%) Y <sub>2</sub> O <sub>3</sub> (5,2±0,2) Al <sub>2</sub> O <sub>3</sub> (<0,4).	Yttria-stabilized tetragonal zirconia polycrystals (Y-TZP)	Innovnano, Portugal

In order to obtain the zirconia particles, zirconia agglomerates as received by the manufacturer were sintered in a furnace (ZircohnZhan, Germany) at 1500°C for 2h. Then, the sintered zirconia was deagglomerated in a mortar. Irregular morphology of the porcelain powders and the spherical-like morphology of the zirconia particles after deagglomeration are shown in Figure 4.1.

Afterwards, the powder mixtures (feldspar-based porcelain and zirconia) were dry ball milled to reduce agglomeration and to enhance mixing. The specimens are hereafter named according to the volume content (xx%) of zirconia (Z) in the porcelain matrix, e.g. Zxx%. Hence, Z0 will stand for pure feldspathic porcelain; Z10 for 10% of zirconia, and so on.

The size distribution of the porcelain and zirconia powders were the following: Porcelain: D<sub>10</sub>= 2.49 µm; D<sub>50</sub>=18.92 µm; D<sub>90</sub>=50.71 µm and D<sub>ave</sub>=23.47 µm; Zirconia: D<sub>10</sub>=14.54 µm; D<sub>50</sub> =162.64 µm; D<sub>90</sub>=336.71 µm and D<sub>ave</sub>=166.44 µm. Figure 4.1 shows the morphology of the powders. Zirconia powders show



**Fig. 4.1** SEM micrograph of feldspathic porcelain powders (A) and zirconia sintered particles (B).

Figure 4.1 shows the irregular morphology of the feldspathic porcelain powders and the spherical-like morphology of the zirconia powders after deagglomeration.

## 2.2. Composites processing

The different mixtures of porcelain and zirconia powders (Figure 4.1) were placed in a graphite die, previously painted with zirconia to avoid direct contact between the powder mixtures and graphite die. The samples were prepared using the heat pressing technique with ~7 MPa of pressure, under vacuum and 970°C during 2 min. Rectangular specimens with 36 x 6 x 2.5 mm were synthesized for 3-point bending tests.

## 2.3 Chemical and Microstructural Characterization

The embedded samples in resin epoxy should first be hand polished on wet sanding paper (SiC), grain #180. Then the surface should be ground with increasingly fine grain sand papers, from 320, 600, 800, 1200, 2500 and ultimately to 4000. The final surface were polished up to mirror using a diamond paste (1 μm) and performed the microstructural characterizations. The microstructural inspection were performed by field emission guns scanning electron microscopy (FEG-SEM NOVA 200 Nano SEM, FEI Company). The atomic contrast images were performed using a Backscattering Electron Detector (BSED)

at an acceleration voltage between 15 and 20 kV. Chemical analyses of specimens were performed by Energy Dispersive Spectroscopy (EDS) technique, using an EDAX Si(Li) coupled to the FEG-SEM

X-ray diffraction (XRD) (AXS D8 Discover, Bruker, Massachusetts, USA) was used to characterize the crystal structure of the zirconia particles present in composites. XRD data were collected in the area  $2\theta = 15$  to  $70^\circ$  with a step of  $0.02^\circ$  using the Cu-K $\alpha$  radiation source and interaction time of 1,2 s.

## 2.4. Mechanical tests

The flexural strength of porcelain-zirconia composites was assessed by a three-point bending test performed in an universal testing machine (Instron 8874, MA, USA). Tests were carried using a load cell of 25kN capacity under a crosshead speed of 0.5mm/s, until fracture. Flexural strength of specimens was calculated as an average of ten specimens tested for each composition ( $n = 10$ ).

The mean values of microhardness of the materials were obtained from 10 indentations for each specimen. The indentations were performed using a Vickers hardness indenter (9,8N) (EmcoTest-DuraScan, Struers, Denmark) with a standard  $136^\circ$  pyramidal diamond (HV<sub>1</sub>), oriented perpendicular to the surface of the specimen. The fracture toughness (K<sub>IC</sub>) of specimens was determined by direct measurement of radial crack length generated by indentation of the specimens on 9.8 N load. The following equation was used (Blendell 1979):

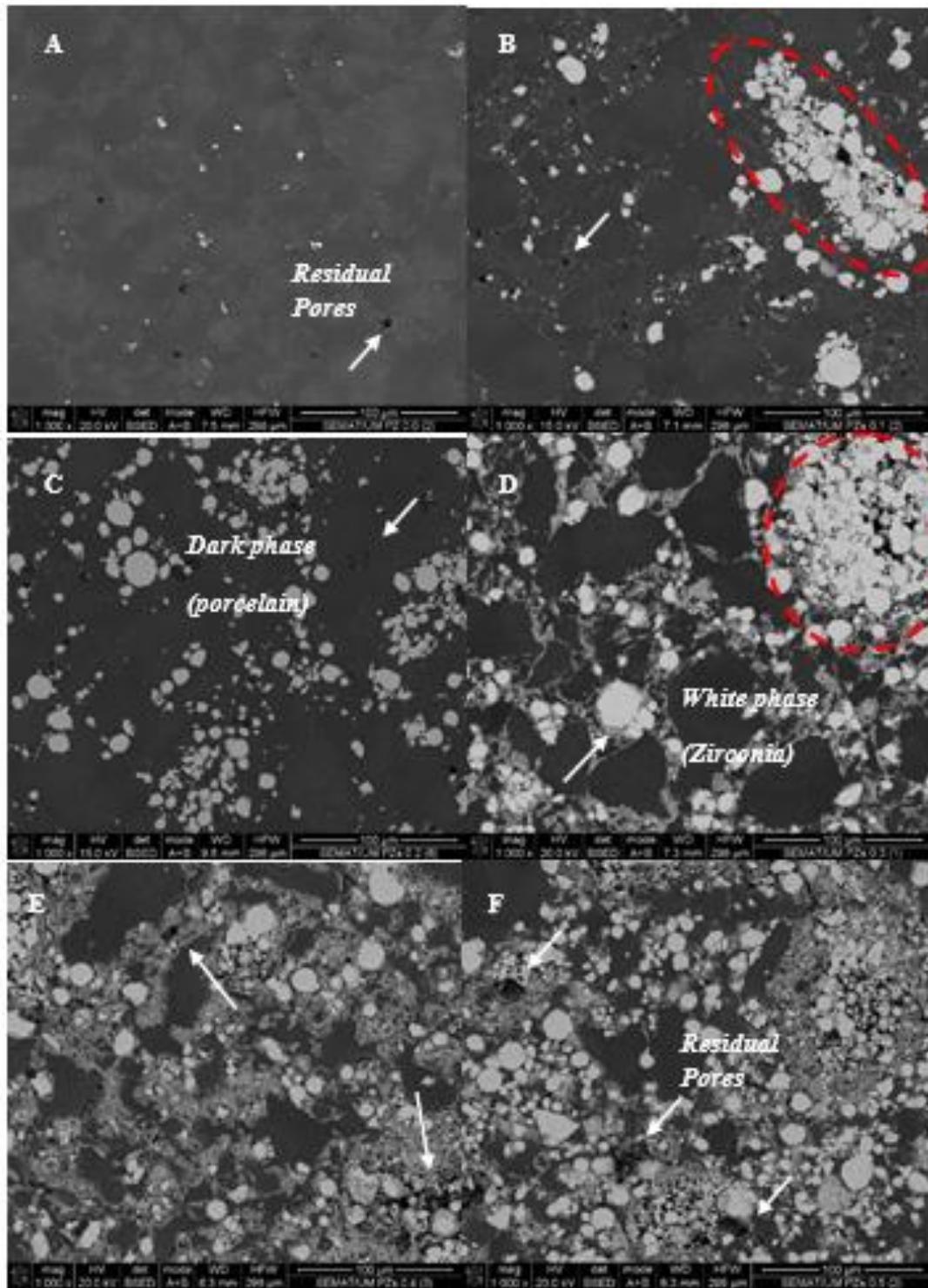
$$K_{IC} = \frac{H_0\sqrt{a}}{\varphi} \left[ 0.055 \log \left\{ \frac{8.4a}{c} \right\} \left\{ \frac{H_0}{E\varphi} \right\}^{-0.4} \right]$$

where:  $\square$

K<sub>IC</sub> = Fracture toughness (MPa·m<sup>1/2</sup>); H<sub>0</sub> = Vickers hardness (GPa); a = half of the diagonal legth of the Vickers indentation (μm); c= half average of crack length (μm); E= Young's modulus (GPa); φ= constant value (3).

### 3. Results

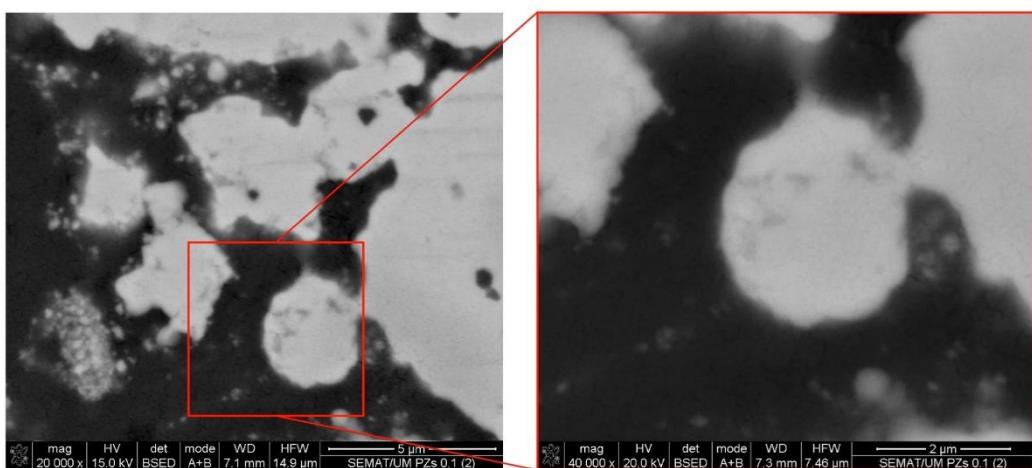
Figure 4.2 shows the microstructure of the feldspar-based porcelain and feldspathic porcelain-zirconia composites containing from 10 up to 50% (vol.%) of zirconia particles.



**Fig. 4.2 –** FEG-SEM images on (A) feldspar-based porcelain and (B) Z10, (C) Z20, (D) Z30, (E) Z40 and (F) Z50 porcelain-zirconia composites. White arrows indicate residual pores. Dashed lines signalize

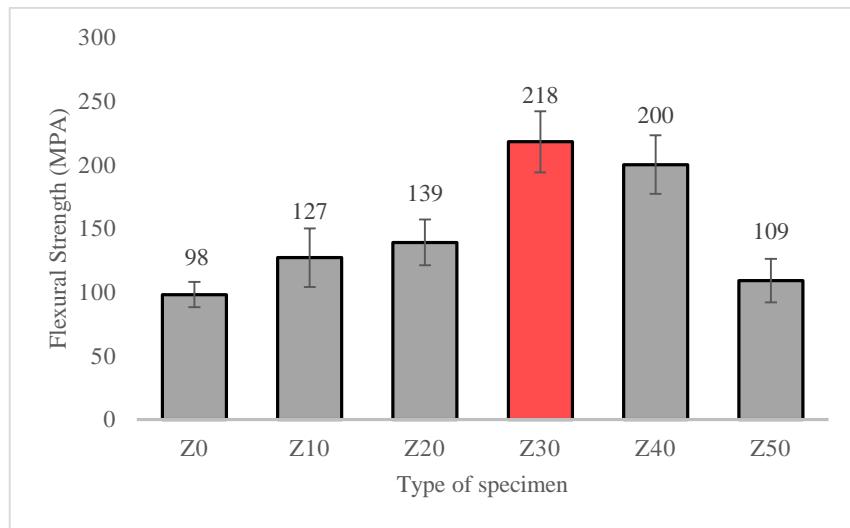
zirconia agglomerates. The porcelain matrix exhibits a dark color and the zirconia particles appear as the white phase.

The feldspathic porcelain matrix exhibits a dark color and the zirconia particles appear as the white phase. Residual pores can be seen in the microstructure of all materials. The segregation of the zirconia smaller particles in feldspathic porcelain was noticed by the presence of a white phase that increases with the volume content of zirconia in the composite (Z10-Z50). Isolated zirconia particles' agglomerates of  $\sim 150$   $\mu\text{m}$  in size can be seen on the micrographs (Figure 4.2B and 4.2D). The bonding between the matrix and the zirconia particles is apparent on the micrographs in Figure 4.2. A flawless interface between zirconia particles and porcelain is shown in Figure 4.3. Additionally, the porcelain was able to fill all the irregularities of the zirconia particles.



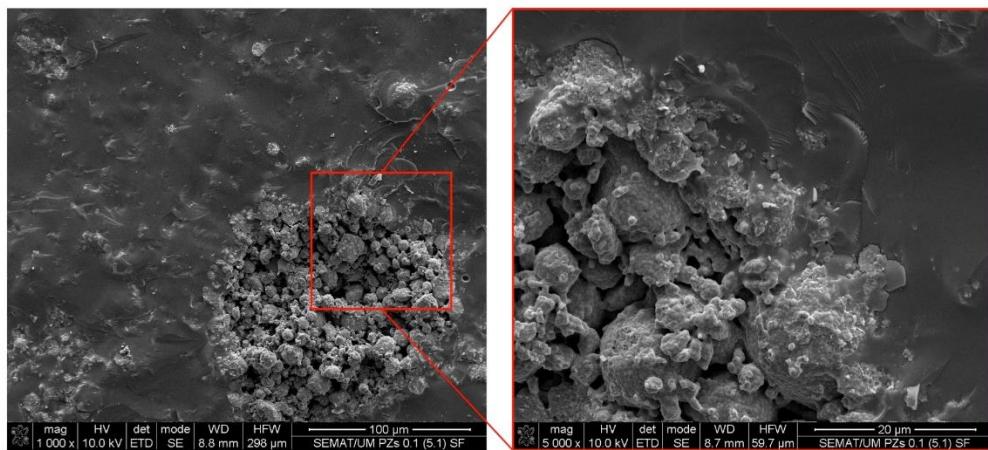
**Fig. 4.3 –** FEG-SEM images revealing details of the interface between the porcelain matrix (dark phase) and the zirconia reinforcing particles (white phase).

The flexural strength results are plotted in Figure 4.4. It was observed an increase in flexural strength of porcelain-zirconia composites with the increasing content of the zirconia particles. The maximum flexural strength value of 218 MPa was reached for composites containing 30% (vol.%) zirconia particles (Z30). For higher zirconia contents in the composite, the flexural strength starts to drop (Z40 and Z50).



**Fig. 4.4** - Flexural strength mean values recorded on porcelain matrix composites containing different volume contents of zirconia phase.

The fractures surfaces of the specimens were also analyzed and they confirmed the proper bond strength between the porcelain matrix and the zirconia particles. The fracture surface of a Z10 specimen is shown in Figure 4.5. A zirconia agglomerate was also inspected to confirm the bonding between the materials. In fact, zirconia particles were veneered by the porcelain, indicating cohesive fracture within the porcelain matrix.



**Fig. 4.5** – FEG-SEM images revealing the fracture surface of a zirconia specimen containing 10% zirconia particles (Z10). (B) Interface between the porcelain matrix and a zirconia particle agglomerate.

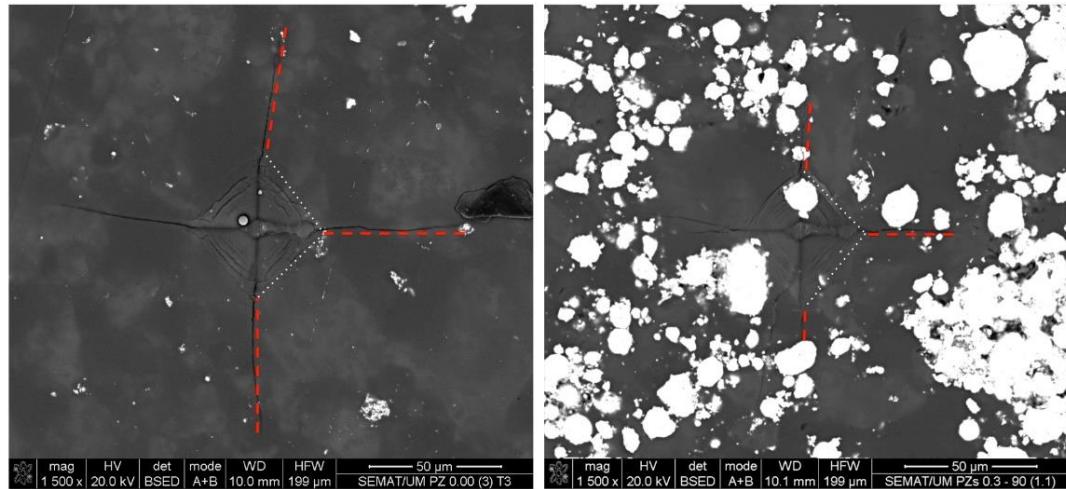
The hardness (HV/GPa) and fracture toughness ( $\text{MPa}\cdot\text{m}^{1/2}$ ) results of feldspar-based porcelain and porcelain-zirconia composites are given in Table 4.2. It was observed a steady increase of the hardness values with the increasing content of zirconia phase up to

30% (vol.%) – Z30. A decrease in hardness was observed for groups Z40 and Z50. On the other hand, the fracture toughness increased with the zirconia content.

A Vickers indentation on the feldspar-based porcelain and porcelain-zirconia composite is shown in Figure 4.6. The crack propagation at the edge of the indentation is clearly seen on the two micrographs. They showed significantly different lengths, which are directly related to the fracture toughness of the material and therefore to its ability to absorb energy prior to rupture.

**Table 4.2** - Hardness (GPa) and Fracture toughness ( $K_{IC}$ ) of feldspar-based porcelain (Z0) and porcelain-zirconia composites (Z10, Z20, Z30, Z40, Z50).

Group of specimens	Hardness [HV/GPa]	Fracture toughness [MPa·m <sup>1/2</sup> ]
<b>Z0</b>	591/5.8	0.9
<b>Z10</b>	613/6.0	1.1
<b>Z20</b>	622/6.1	1.5
<b>Z30</b>	661/6.5	2.1
<b>Z40</b>	615/6.0	2.1
<b>Z50</b>	608/5.9	2.7

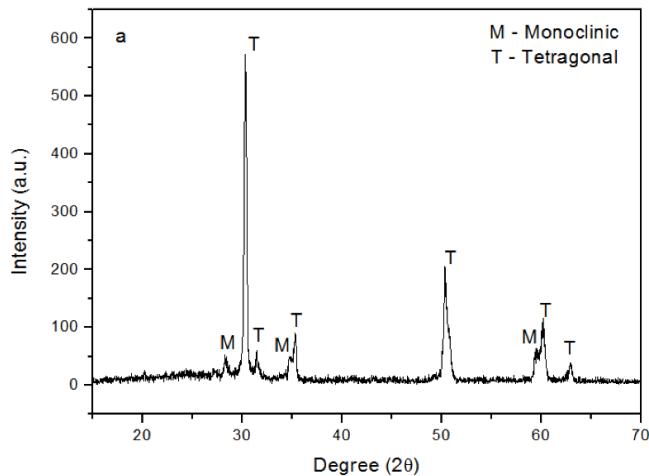


**Fig. 4.6** – Vickers indentation with induced crack propagation in (A) feldspar-based porcelain and (B) Z30 composite.

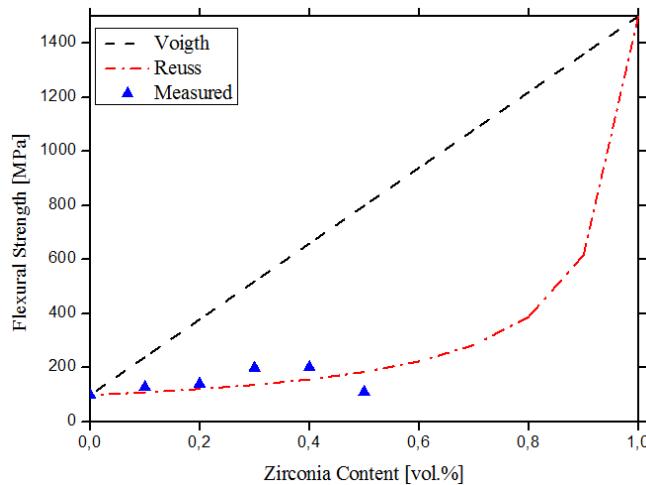
The XRD pattern of the feldspathic porcelain-zirconia composite containing 30% (vol.%) zirconia particles is shown in Figure 4.7. Peaks of 82% tetragonal zirconia and 18% monoclinic zirconia were detected by XRD analysis. It was not observed a variation on the amount of monoclinic phase after composites processing. The tetragonal

to monoclinic transformation occurred during the mechanical deagglomeration process undergone by the zirconia powders after the pre-sintering treatment.

The flexural strength of the feldspathic porcelain-zirconia composites as compared to the values estimated by the rule of Voigt and Reuss models are plotted in Figure 4.8. The experimental values followed closely those estimated by Reuss model.



**Fig. 4.7** X-Ray diffraction pattern of the feldspathic porcelain-zirconia composite, Z30.



**Fig. 4.8** Plot of the flexural strength of feldspathic porcelain-zirconia composites as compared to the rule of mixtures models, Voigt and Reuss.

#### **4. Discussion**

Feldspathic porcelain has been for long time the veneering material of choice used in metal-ceramic and all-ceramic dental restorations. However, it lacks in mechanical strength when compared to the underlying materials and therefore its mechanical properties could be desirably improved. The incorporation of zirconia as reinforcing phase has been successfully carried out to improve the mechanical properties of different materials (Asopa et al 2015; Huang et al 2014; Korkmaz et al 2005; Verné et al 2003;; Panyayong et al 2002; Zuccari et al 1997;). Zirconia has been the selected for the reinforcing phase due to its excellent mechanical properties, corrosion resistance, biocompatibility, aesthetics and thermal compatibility to zirconia substructures of dental prostheses (Piconi and Maccauro 1999).

In this work, the fabrication of porcelain-zirconia composites was successfully achieved, using the heat pressing technique to minimize the defects such pores and flaws in the specimens (Henriques et al 2014; Henriques et al, 2012; Henriques et al, 2012b; Henriques et al 2011;). The pre-sintering of the zirconia agglomerates supplied by the manufacturers intended to produce bigger and dense particles that could be used as a reinforcing phase, thus having load bearing capacity.

The addition of non pre-sintered zirconia agglomerates to feldspathic porcelain composites had been studied and showed significantly lower mechanical properties than those obtained in this study (Verné et al, 2003). The addition of zirconia particles to porcelain has produced the general effect of increasing fracture strength, hardness and toughness. This finding is in accordance with other studies that used a stronger ceramic phase to strengthen a typically weaker ceramic (e.g. glass or porcelain) or polymer (e.g. PMMA) (Asopa et al 2015; Huang et al 2014; Korkmaz et al 2005; Verné et al 2003;; Panyayong et al 2002; Zuccari et al 1997;).

The microstructure analyses showed a well distribution of zirconia particles although zirconia agglomerates and residual pores were found in the microstructure of all specimens. Both zirconia agglomerates and small pores, produced by entrapped air during porcelain fusing, were considered flaws. The agglomeration can be traced to the preparation of the zirconia powders that were obtained out of the pre-sintering of the spherical zirconia agglomerates ( $<60 \mu\text{m}$ ) supplied by the manufacturer. After this process, the deagglomeration of the pre-sintered powder was performed but some zirconia agglomerates ( $\sim 150 \mu\text{m}$ ) remained in the powder. The preparation of powder is crucial

for achieving composites with high strength and, for future iterations, the larger agglomerates should be removed from the powder.

The increase in flexural strength confirms that a good bonding between the two phases of the composites was achieved and suggests that a load-transfer mechanism can be active. The significant load transfer strengthening requires that the Young's modulus of the reinforcing phase should be at least twice of that of the matrix as well as by the proper bonding between the two phases. The coefficient of thermal expansion (CTE) of the reinforcing phase should not be significantly higher to that of the matrix avoiding high stresses which could lead to the interfacial debonding and micro cracking. That could decrease the fracture stress. All these conditions are confirmed in porcelain-zirconia composites.

The crack deflection (Faber and Evans, 1983; Faber and Evans, 1983a) and crack bridging (Cook et al 2011) were the toughening mechanisms observed in the composites. The crack deflection was observed by the presence of feldspathic porcelain material covering the zirconia particles at the fracture surface (Figure 4.5). This shows that crack did not propagate through the zirconia particle. Instead it was deviated around it due to the high strength of the zirconia particle and the good bonding between the reinforcement and the matrix. Additionally, the fracture mode, which was determined by FEG-SEM examination of fracture surfaces of the composites, showed mainly cohesive fracture type within the porcelain. The crack bridging from particles was observed at the zirconia agglomerates, in which mechanical strength are lower than that of the smaller zirconia particles. This was also evidenced by damaged zirconia agglomerate (Figure 4.4). No pull outs of the zirconia particles were noticed.

The fracture toughness,  $K_{IC}$ , is the critical stress intensity level at which a given flaw starts extending and provides insight on the potential resistance to crack growth of a material (Wang et al, 2005). However, the measurement of  $K_{IC}$  is much sensitive to the technique and procedures (Wang et al, 2005). The fracture toughness values recorded for feldspar-based porcelain is in accordance with those reported in other studies 0.9-1.0 MPa.m<sup>1/2</sup> (Rizkala et al, 2004). The flexural strength of the Z10-Z40 composites are contained in the boundaries of Voigt and Reuss mixing rules. The flexural strength values recorded for Z10 and Z20 were well predicted by Reuss rule while the values for Z30 and Z40 composites were slightly above Reuss line. On the other hand, the flexural strength values for composites Z50 were slightly bellow the Reuss line.

The Young's moduli values of the composites were higher than that of feldspar-based porcelain. Also, those values increased with the increasing amount of zirconia phase in the composite. The trend observed in this study is in agreement with other studies on glass- or porcelain-matrix composites containing reinforcement particles. Such improvements in the strength and toughness are often associated with an increased Young's modulus (Henriques et al, 2014; Frey and Mackenzie 1967).

The benefits of the introduction of zirconia particles as reinforcing phase of dental porcelain have been demonstrated in this study. The authors are conducting further studies on the wear behavior and on the influence of the zirconia particles size on the mechanical properties of porcelain-zirconia composites. Together with mechanical strength and wear behavior, the aesthetic properties of dental materials are also very important. Therefore, colorimetric tests should also be performed.

## 5. Conclusions

In this study, the microstructure and mechanical properties of porcelain-zirconia composites containing up to 50% (vol.%) zirconia have been evaluated.

The addition of zirconia phase showed to improve the overall mechanical properties of porcelain. The highest values of flexural strength and fracture toughness were obtained for composites containing 30% (vol.%) of zirconia particles. The flexural strength and fracture toughness were increased by >100%, and hardness by 12% relative to feldspar-based porcelain values. The enhanced properties displayed by such composites can provide a high performance for dental prostheses.

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## **CHAPTER V**

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### **Wear performance of feldspathic porcelain reinforced by zirconia agglomerates and by zirconia particles**

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#### **Abstract**

The aim of this paper was to examine the wear behaviour of a dental feldspathic porcelain reinforced by Yttria-Stabilized Zirconia (3Y-TZP). Dental feldspathic porcelain composites were reinforced by 20% (vol. %) zirconia. Two types of particles were tested: zirconia agglomerates and pre-sintered zirconia particles. Feldspathic porcelain and zirconia reinforced feldspathic porcelain composites were produced by heat pressing. The reciprocating ball-on-plate wear tests were performed in saliva artificial solution at 37 °C, at 30 N normal load, 1 Hz and stroke length of 3 mm. The dominant wear mechanisms were characterized by field emission guns scanning electron microscopy. Results revealed an improvement of wear behavior for dental feldspathic porcelain reinforced by 20% (vol.%) pre-sintered 3Y-TZP. Such improvement on wear resistance was attributed to the effect of reinforcement (improving the grain-boundary strength), by the action of the uniformly distributed pre-sintered zirconia particles. That allowed the load transfer reinforcing mechanism through the matrix and reinforcement phase.

**Keywords:** glass-ceramic; zirconia; composite; dental restoration; wear.

## **1. Introduction**

All-ceramic restorations have been considered a good alternative to overcome the tribocorrosion processes occurring on metal-based materials. Ceramic veneers are used for prosthetic restorative materials based on optical properties, which provide proper aesthetic results (Friedman et al 1991; Kelly 1997; Rosenblum ad Schulman 1997; Yen et al, 2001; Fisher et al 2002). The main problems reported by in vivo and in vitro studies are poor mechanical properties (low tensile strength, low fracture toughness) and brittleness (Kelly 1997; Kelly et al, 1996; Chevalier et al, 2009). Any small defect in a dental glass-ceramic might represent a stress concentration point from where a crack can propagate, leading to fracture.

Nowadays zirconia is one of the best choices for dental restorations due to their mechanical and corrosion properties (Stachowiak et al 2000; Mitov et al 2012; Manicome et al, 2007). They have high mechanical strength, increased fracture toughness, good thermal expansion coefficient, good oxidation resistance and low thermal conductivity, good biocompatibility, low radioactivity, tooth like optical properties (Stachowiak et al 2000; Mitov et al, 2012). The mechanical properties of Y-TZP are superior to any other ceramic materials. For example, it have been reported that in-vitro flexural strengths range from 900 to 1200 MPa and the fracture toughness ranges from 9-20 MPa (Figueiredo-Pina et al 2013). The main problems reported regarding the use of zirconia in dental application are: (i) lack of transparencies (Yamashita et al, 2012) and (ii) it wears the opposite tooth or restauration (Mitov et al, 2012; Figueiredo-Pina et al, 2013; Kim et al, 2012; Sabrah et al, 2013).

In order to use feldspathic porcelain in load-bearing applications, it is necessary to enhance their mechanical, fatigue and wear properties. Thus, the addition of a second high-strength biocompatible phase into the glass-ceramic matrix can optimize the properties of the resultant material (Ferraris et al, 1996; Verné et al, 1998; Verné et al, 2000; Kasuga et al, 1992; Kasuga et al, 1998; Denry et al, 1996; Seghi et al 1995; Krejci et al, 1994; Schwickerath 1992; Krejci 1991; Hamouda and Beyari, 2013). Glass-ceramics have been reinforced by alumina or zirconia (e.g. Yttria-Stabilized Zirconia) to improve wear resistance, optical properties and biocompatibility (Denry et al, 1996; Seghi et al, 1995; Krejci et al 1994; Schwickerath 1992; Krejci 1991; Hamouda and Beyari, 2013; He et al, 1997; Nicola et al, 2008).

Guazzato et al. (Guazzato et al, 2004) reported that the zirconia reinforced feldspathic porcelain composites are stronger and tougher materials than the conventional feldspathic porcelain. The improvement on the properties of the zirconia reinforced feldspathic porcelain composites was attributed to phase transformation from tetragonal to monoclinic and to the relationship between the glassy matrix and the crystalline second phase in the strengthening and toughening mechanisms of these ceramics. The strengthening mechanisms of zirconia reinforced glass-ceramic composites are based on stopping, deflection or bridging the crack propagation (Guazzato et al 2004; Scherrer et al, 1998; Medeiros et al, 2009), either, on compressive residual stresses due to thermal mismatch between the glass-ceramic matrix and inorganic fillers. It has been mentioned that the optimization of the microstructure is an important factor for improvement on friction and wear behavior of dental glass-ceramic (He et al, 1997; Yu et al, 2006). As stated by He et al. (He et al, 1997), the amount of tetragonal zirconia transformed to the monoclinic crystal structure increased with increasing grain size resulting in a decrease in wear resistance. The volume increment caused by this phase transformation weakens the grain boundaries which results in grain pull-out.

The present study reveals the wear behavior of zirconia reinforced glass-ceramic composites in a saliva artificial solution. It was hypothesized that the addition of pre-sintered yttria-stabilized zirconia particles into glass-ceramic is very effective in reducing the wear loss of the resulting material.

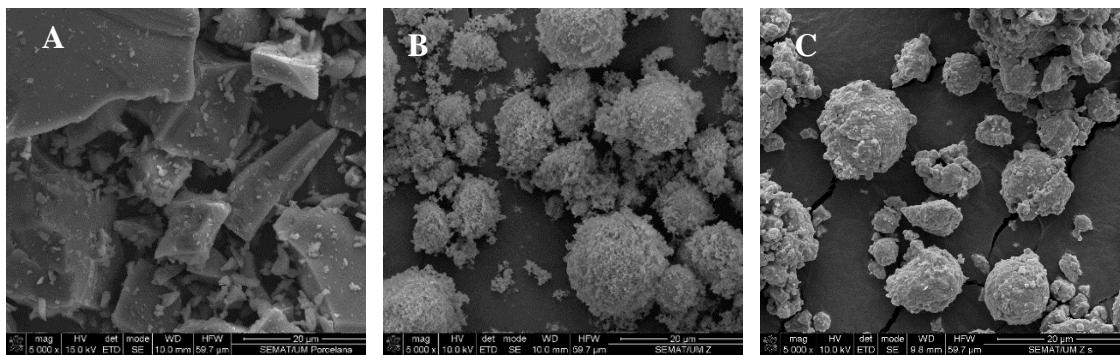
## 2. Experimental procedure

### 2.1. Materials

A dental feldspathic porcelain powder (Vita VM9, Vita, Germany) was used as matrix material. The chemical composition of the glass-ceramic is shown in Table 5.1. FEGSEM images of dental feldspathic porcelain powder (raw material) as provided by the supplier are show in Figure 5.1A. The powder size distribution of feldspathic porcelain powder was  $D_{10}=2.49\text{ }\mu\text{m}$ ;  $D_{50}=18.92\text{ }\mu\text{m}$ ;  $D_{90}=50.71\text{ }\mu\text{m}$  and  $D_{ave}=23.47\text{ }\mu\text{m}$ .

**Table 5.1** Chemical composition of dental feldspathic porcelain powder (wt.%). (VITA®)

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	B <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	Other oxides
60-64	13-15	3-5	7-10	4-6	~2



**Fig. 5.1** FEGSEM images showing: A) Feldspathic porcelain; B) zirconia agglomerates; and C) pre-sintered zirconia powders.

Yttria-stabilized zirconia particles - 3Y-TZP (Innovnano, Portugal), were used as reinforcement (Table 5.2). FEGSEM images of the zirconia agglomerates and pre-sintered zirconia powder are shown in Figure 5.1B and 5.1C, respectively. The powder size distribution of pre-sintered zirconia is  $D_{10}=14.54\text{ }\mu\text{m}$ ;  $D_{50}=162.64\text{ }\mu\text{m}$ ;  $D_{90}=336.71\text{ }\mu\text{m}$  and  $D_{ave}=166.44\text{ }\mu\text{m}$ .

**Table 5.2** Chemical composition of 3Y-TZP powder (wt.%)

ZrO <sub>2</sub> + HfO <sub>2</sub> + Y <sub>2</sub> O <sub>3</sub> + Al <sub>2</sub> O <sub>3</sub>	Y <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	HfO <sub>2</sub>	Other oxides
99.9	5.2±0.2	<0.4	<0.5	<0.5

## 2.2. Fabrication of zirconia reinforced glass-ceramic composites

The feldspathic porcelain was used as matrix material (named as Z0 from now on). Two types of zirconia reinforced feldspathic porcelain composites were produced:

- (i). feldspathic porcelain reinforced by 20% (vol.%) Yttria-Stabilized Zirconia (ZrO<sub>2</sub> – 3% Y<sub>2</sub>O<sub>3</sub>) agglomerates (named as ZA from now on). The 3Y-TZP agglomerates were used as provided by the supplier and blended with the feldspathic porcelain powders were ball milled during 24 h.
- (ii). Feldspathic porcelain reinforced by 20% (vol%) pre-sintered Yttria-Stabilized Zirconia (ZrO<sub>2</sub> – 3% Y<sub>2</sub>O<sub>3</sub>) particles (named as ZP from now on). The 3Y-TZP agglomerates as provided by the supplier were sintered in a furnace at 1500°C for 2h. Afterwards, powder mixtures (feldspathic porcelain and sintered 3Y-TZP), were ball milled to reduce agglomeration and to enhance mixing.

All the samples were processed by the hot pressing (HP) technique (Medeiros et al, 2009; Yu et al, 2006; Souza et al 2013; Sampaio et al 2015; Hutching, 1992; Yin et al, 2003). The compactation pressure applied was 7.0MPa in a stage of 2 minutes at 970°C under vacuum (1 bar).

### **2.3. Microstructural and chemical analysis**

The obtained samples were characterized in terms of microstructure, morphology and chemical composition by Field Emission Guns Scanning Electron Microscopy (FEGSEM) coupled to Energy Dispersive Spectrometer (EDS) (FEGSEM, FEI Nova 200, USA). The samples were sputter-coated with carbon.

### **2.4. Hardness measurements**

Vicker's microhardness measurements were performed on 10 different areas of the samples surfaces ( $n = 50$ ) using a microhardness tester (DuraScan, Emco-Test, Austria) with a load of 1 kgf (9,8N) during 15 s. Vickers hardness mean values were obtained as a average of 10 indentations per sample.

### **2.5. Wear tests**

Square test samples (10 x 10 x 2 mm) were embedded in epoxy resin. Samples were wet ground on SiC sandpapers down to 4000Mesh and then polished using diamond paste (1µm). Samples were ultrasonically cleaned in isopropyl alcohol for 15 min and then in distilled water for 15 min. A reciprocating ball-on-plate tribometer (Bruker-UMT-2) was used to evaluate the wear of square samples (10 x 10 x 2 mm) against Al<sub>2</sub>O<sub>3</sub> counterbody (10 mm diameter alumina ball, Goodfellow). The samples were placed in an acrylic electrochemical cell containing a Fusayama artificial saliva solution (Table 5.3), that was attached to the tribometer.

**Table 5.3** Composition of the stock Fusayama artificial saliva (Fusayama et al, 1963).

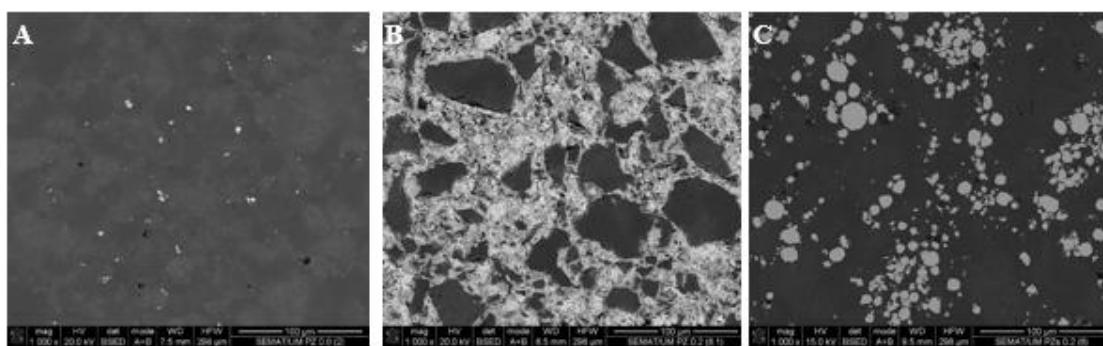
Compounds	g/L
NaCl	0.4
KCl	0.4
CaCl <sub>2</sub> · 2H <sub>2</sub> O	0.795
Na <sub>2</sub> S· 9H <sub>2</sub> O	0.005
NaH <sub>2</sub> PO <sub>4</sub> · 2H <sub>2</sub> O	0.69
Urea	1

The tribological parameters were 30 N normal load, at a frequency of 1Hz, and 3 mm of displacement, during 30 min. A set of five experiments was performed for each test condition. After testing, the specific wear rate was estimated by measuring the lateral width of the wear scars and using empirical mathematical equations assuming that the wear scars are formed by perfect ball geometry (Sampaio et al, 2015). All tests were performed in laboratory environment ( $20 \pm 2^\circ\text{C}$ ).

### 3. Results and discussion

#### 3.1. Microstructural and chemical characterization

FEGSEM images of the microstructure of feldspathic porcelain and zirconia reinforced feldspathic porcelain composites are shown in Fig. 5.2. It can be seen differences on the microstructure of the materials.



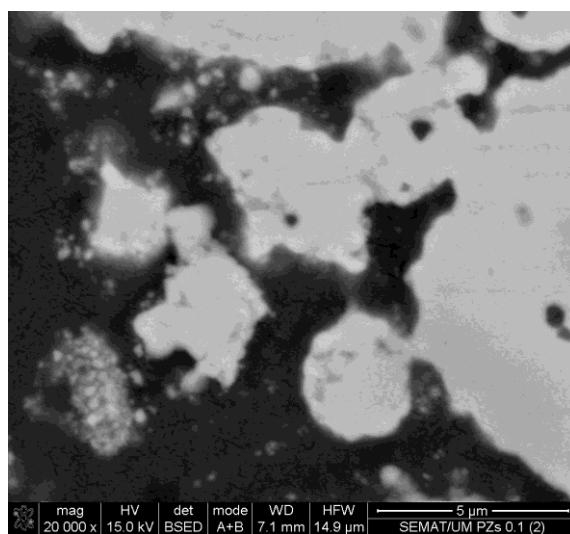
**Fig. 5.2** FEGSEM images of the microstructure of: A) Feldspathic porcelain (Z0); B) Feldspathic porcelain reinforced by zirconia agglomerates (ZA) and C) feldspathic porcelain reinforced by zirconia particles (ZP).

The chemical analysis of the sintered feldspathic porcelain reveals the presence of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>; B<sub>2</sub>O<sub>3</sub>; K<sub>2</sub>O and Na<sub>2</sub>O (Fig 5.2A). Residual porosity can be seen in the micrograph represented by small black dots in the microstructure.

The microstructure of ZA samples and no zirconia agglomerates are noticed in Figure 5.2B. The absence of zirconia agglomerates may be explained based on the fact that they were destroyed during the mixing procedure. The dark phase observed in the microstructure (Fig. 5.2B) is feldspathic porcelain while the white phase is a zirconia rich phase that is composed by smeared zirconia particles mixed with feldspathic porcelain powders in less quantity.

The microstructure of the feldspathic porcelain composites reinforced by pre-sintered zirconia particles is presented in Fig. 5.2C. The white phases are the round zirconia particles that are distributed through the feldspathic porcelain matrix (dark phase). Residual porosity can be observed in the microstructure as small black dots.

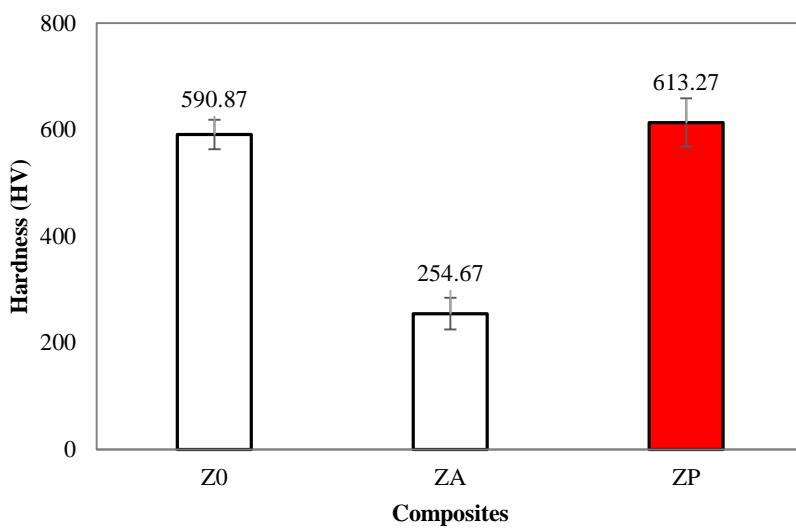
FEG-SEM image (with a higher magnification 20000x) of the feldspathic porcelain composite reinforced by zirconia particles revealed details of the interface between the reinforcement and matrix phases. It can be observed a good infiltration of the feldspathic porcelain into the zirconia particles details.



**Fig. 5.3** Detailed view of the FEGSEM interface between the zirconia particles (white phase) and the feldspathic porcelain matrix (dark phase).

### 3.2. Hardness values

The hardness mean values recorded on the test samples area shown in Figure 5.4. The mean hardness value recorded for the feldspathic porcelain samples was  $591 \pm 3$  HV, while ZA samples revealed values at  $255 \pm 3$  HV and ZP at  $622 \pm 5$  HV. The ZA samples showed a substantial decrease (by 57%) on hardness value, while the ZP samples showed a slight increase (by 5%), as compared to the feldspathic porcelain.



**Fig. 5.4** Hardness of the feldspathic porcelain and zirconia reinforced feldspathic porcelain composites.

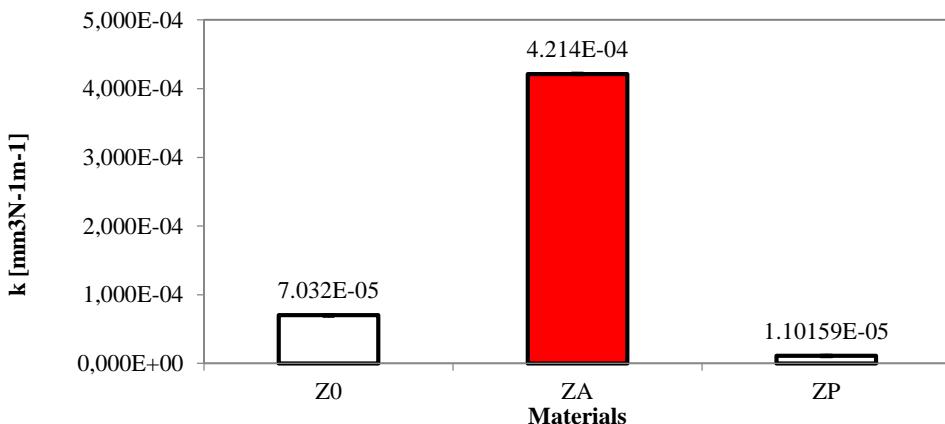
### 3.3. Specific wear rate

The specific wear rates for feldspathic porcelain and zirconia reinforced feldspathic porcelain composites are shown in Fig. 5.5.

The wear performance was strongly influenced by the type of reinforcement phase that was used in each material: zirconia agglomerates (ZA) or particles (ZP), as compared to the feldspathic porcelain.

The highest specific wear rate was recorded on the feldspathic porcelain reinforced with zirconia agglomerates (ZA). The pre-sintering of zirconia powders revealed a positive effect on the decrease of the wear resistance as compared with both feldspathic porcelain and feldspathic porcelain composites reinforced by zirconia agglomerates (ZA). In this study, the wear results corroborate the results obtained for

hardness tests (Fig. 5.4). Also, Yin et al. have also reported a correlation between the wear rate and hardness from their results (Yin et al, 2003).



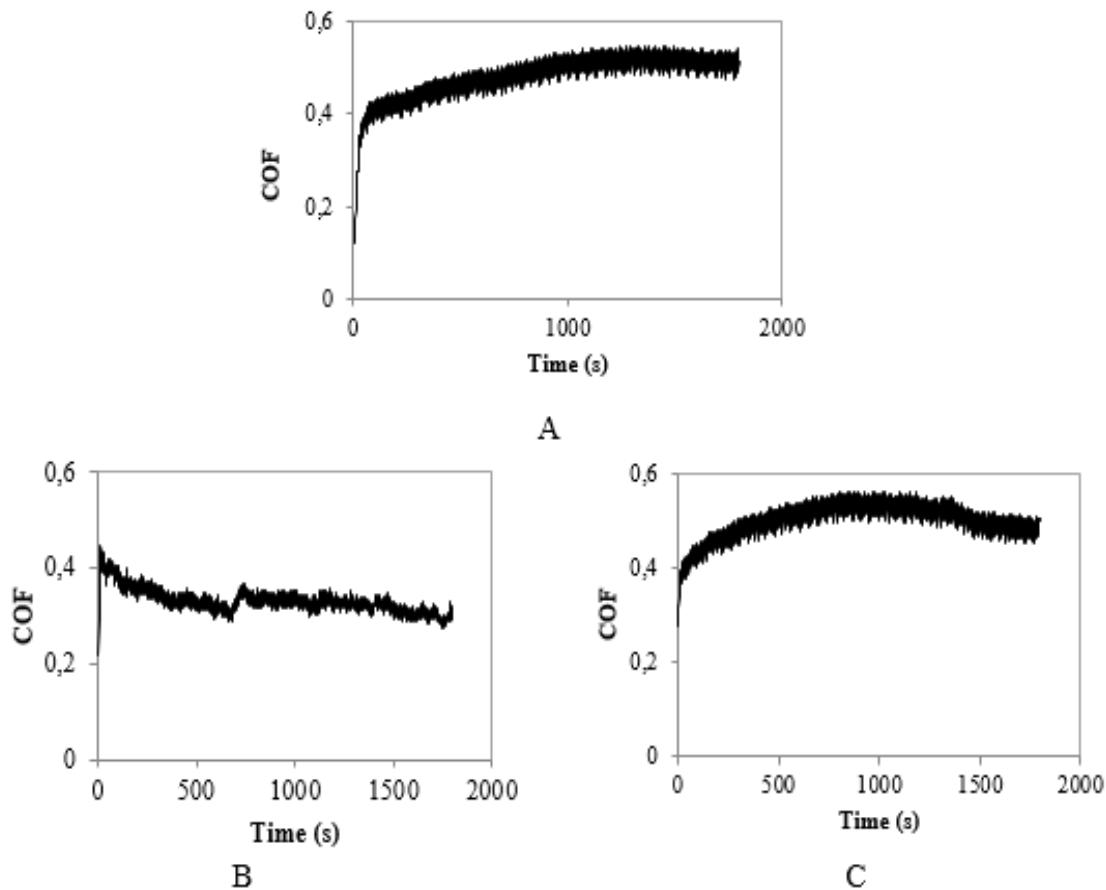
**Fig. 5.5** Specific wear rate of the feldspathic porcelain and zirconia reinforced feldspathic porcelain composites.

It has been stated that the environment has also a significant influence on the wear behaviour of feldspathic porcelains based on the interactions of their microstructural components with the environment. The hardness and consequently the wear rate values of feldspathic porcelain decreases in an aqueous environment. In the presence of saliva the two contact materials can easily adhere at the microscopic level of sharp asperities (Yin et al, 2003; Monasky and Taylor, 1971).

### 3.4. Coefficient of friction

The evolution of the coefficient of friction (COF) during sliding for feldspathic porcelain and zirconia reinforced feldspathic porcelain composites against Al<sub>2</sub>O<sub>3</sub> ball in saliva artificial solution is shown in Fig.6.

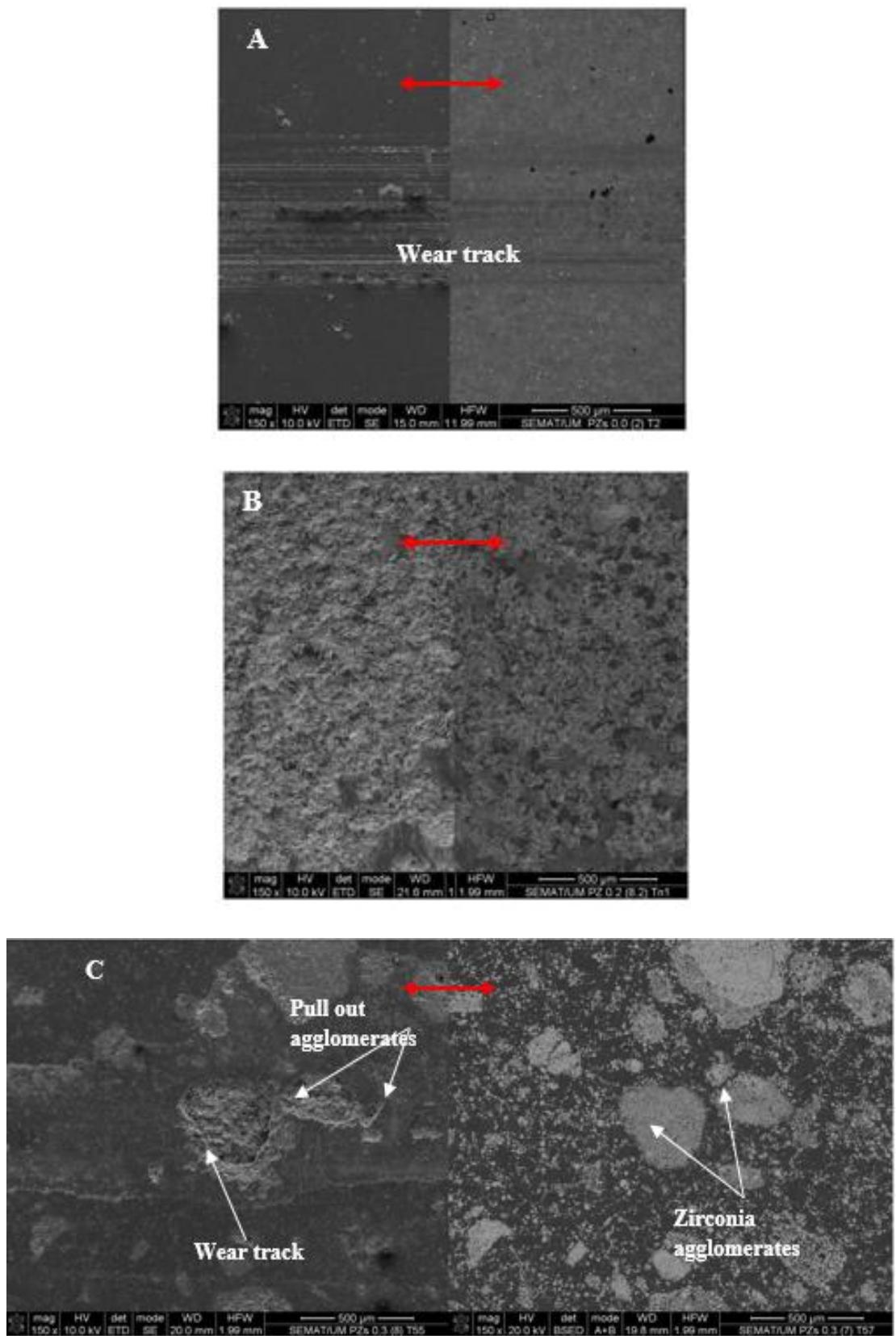
The COF value of the feldspathic porcelain and zirconia reinforced feldspathic porcelain composites attains the steady-state regime after a very short running-in period. Concerning the COF mean values during the steady state regime, no significant difference was found between those test samples. A slight decrease in COF was observed in the case of the feldspathic porcelain composite reinforced with zirconia agglomerates. This may be explained mainly by the lack of cohesion of the zirconia agglomerates verified in the ZA samples, which makes that zirconia particles pull out to the wear track. This fact could be confirmed by the presence of a white “slurry” surrounding the wear track after the sliding test.



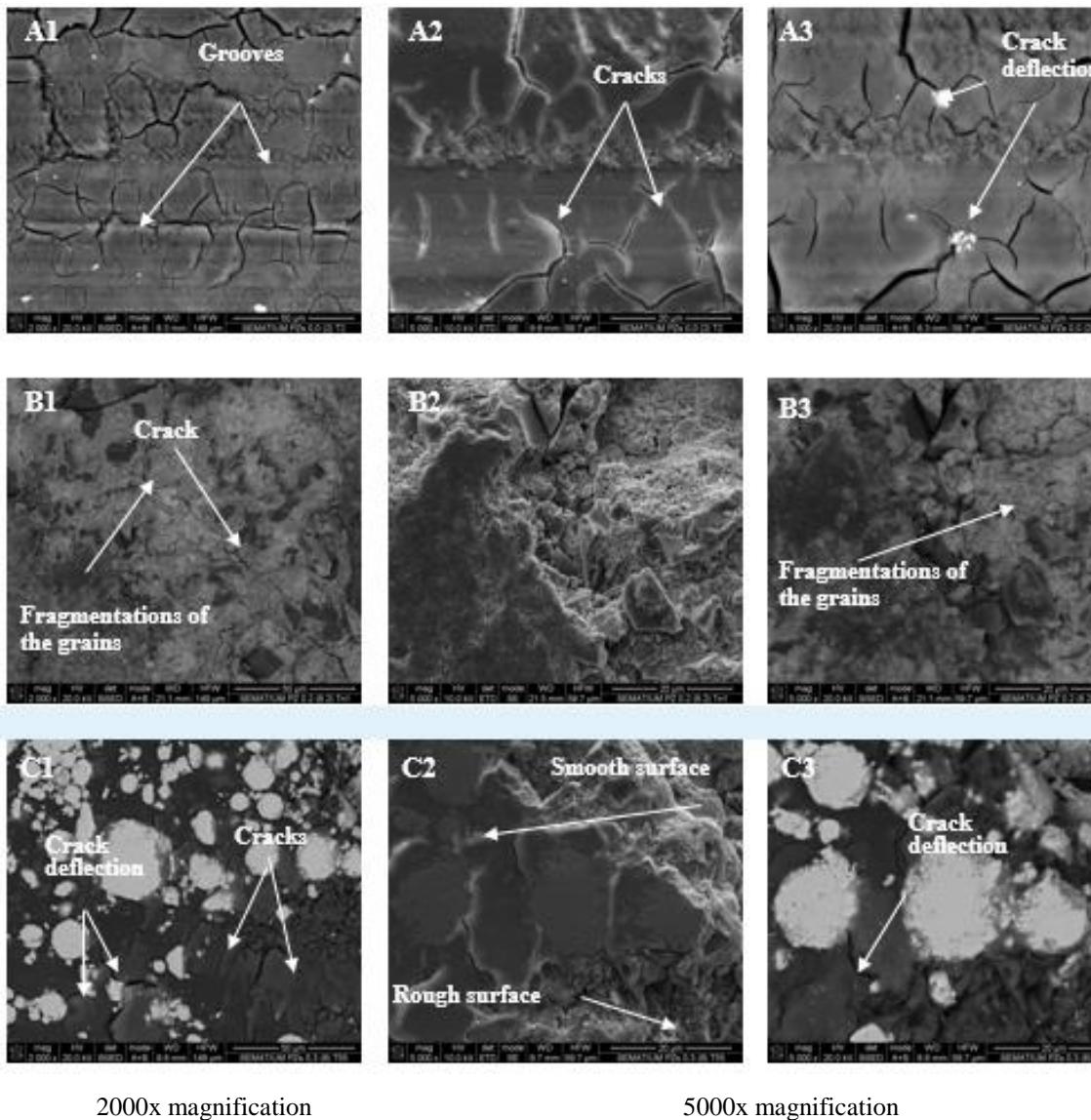
**Fig. 5.6** Evolution of COF along the time for: A) Feldspathic porcelain (Z0); B) Feldspathic porcelain composite reinforced with zirconia agglomerates (ZA) and C) Feldspathic porcelain composite reinforced with zirconia particles (ZP).

### 3.5. Microscopic analysis on worn surfaces

FEGSEM images of the wear tracks after reciprocating sliding tests of both feldspathic porcelain and zirconia reinforced feldspathic porcelain composites against alumina immersed in artificial saliva are shown in Figures 5.7 and 5.8. The sliding directions, are indicated by the arrows on the micrographs (Fig. 5.7).

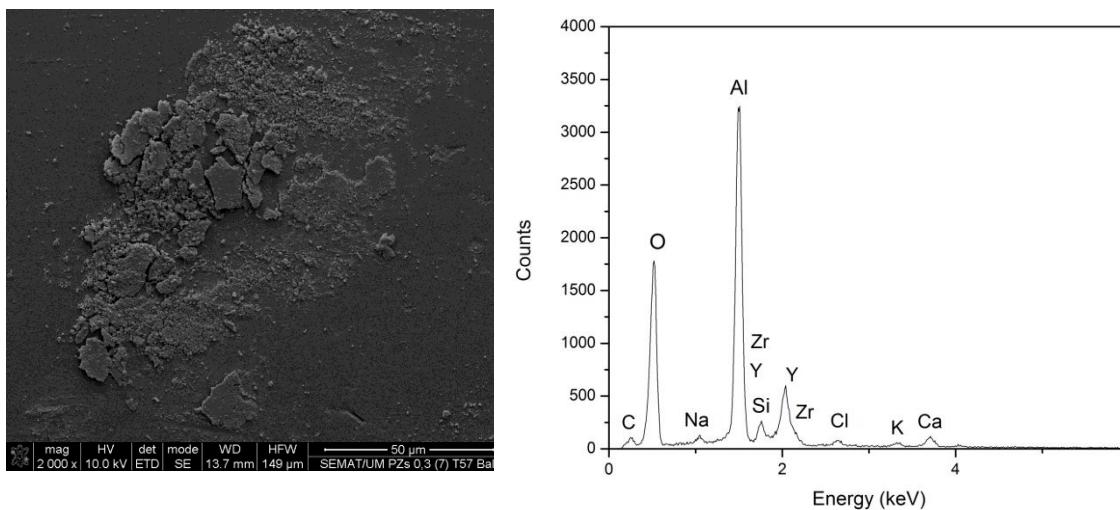


**Fig. 5.7** FEGSEM images of the middle area of the wear track: A) Feldspathic Porcelain (Z0); B) Feldspathic porcelain composite reinforced with zirconia agglomerates (ZA) and C) Feldspathic porcelain composite reinforced with zirconia particles (ZP).



**Fig. 5.8** FEGSEM images of the wear track: A) glass-ceramic (Z0); B) glass-ceramic composite reinforced with zirconia agglomerates (ZA) and C) glass-ceramic composite reinforced with zirconia particles (ZP).

FEGSEM images and EDS spectra of the counter material (alumina ball) surfaces after sliding against the test samples are shown in Fig. 5.9. EDS analysis revealed material transfer from the ZP samples to the alumina ball, suggesting an adhesive wear mechanism. Also, EDS analysis revealed the presence of Al and O from the alumina ball as well as Zr, Y and Si coming from the zirconia reinforced feldspathic porcelain composites. The presence of C, Na, Cl, K, Ca can be attributed to the feldspathic porcelain and artificial saliva constituents.



**Fig. 5.9** FEG-SEM images of the Al<sub>2</sub>O<sub>3</sub> ball after sliding against feldspathic porcelain composite reinforced by zirconia particles (ZP) samples.

Regarding the worn surface morphology of feldspathic porcelain and zirconia reinforced feldspathic porcelain composites; different wear mechanisms were noted by FEGSEM analysis (Figs. 5.7 and 5.8).

The sliding scratches can be observed only on the feldspathic porcelain samples (Figs. 5.7A and 8A), being attributed to the abrasive wear caused by the transferred material to the ball. Also, it can be noticed multiple cracks through the wear track, which is a typical wear feature of the feldspathic porcelain as they are brittle and the wear of their surface occurs by fracture (Oh et al, 2002).

The largest wear track area was detected for ZA samples (Fig. 5.7B), evidencing a surface damage acceleration relative to the other samples. The ZA micrographs did not reveal the presence of zirconia agglomerates (Fig. 5.2), suggesting their destruction during the mixing procedure. As previously mentioned, the white phase in Fig. 5.2 (and also in Fig. 5.8B) corresponds to the zirconia powder that covered the feldspathic porcelain powders and negatively impacted the sintering of the composite. Most of the feldspathic porcelain powders were covered by fine zirconia particles that sintered at 1500°C and not at 970°C as happens with glass-ceramic.

The worn surface of the composite reinforced by zirconia agglomerates showed a lot of peaks and valleys resultant from delamination. It can be observed from FEGSEM images with a higher magnification (Fig. 5.8B) that the grains/particles were fragmented. It is possible that fragments from the samples contribute to the formation of the third body abrasive particles and consequently to an increase on volume loss.

On the other hand, regarding the feldspathic porcelain reinforced with zirconia particles (ZP) it can be seen from the micrographs the round zirconia particles very well

dispersed through the feldspathic porcelain matrix (Fig. 5.2). The zirconia particles act as a second phase that is stiffer than the feldspathic porcelain matrix, allowing the load transfer reinforcing mechanism to occur from the matrix to the reinforcing phase. There was a good bonding between the zirconia particles and the feldspathic porcelain matrix (Fig. 5.3) that may explained the increased extension of smooth surface noted on the worn surface of the P/ZP samples (Figs. 5.7C and 5.8C) and consequently the improvement on wear performance (Fig. 5.4). The presence of some voids was detected on the worn surfaces of the P/ZP samples. These voids resulted mainly from the pull out of zirconia larger particles and particles agglomerates as seen in the backscattered FEGSEM images of the worn surfaces (Fig. 5.7c).

It is well known that the particles agglomerates are critic areas from the point of view of wear resistance and mechanical strength. It is important to point out that less cracks were observed on the worn surface of ZP samples (Fig. 5.7), as compared to the feldspathic porcelain (Fig. 5.8). This is explained by the toughening effect produced by the dispersed zirconia particles in the feldspathic porcelain matrix. Hence, when a crack arises in the weaker matrix (feldspathic porcelain) it is deflected or blocked due to the presence of a stronger zirconia phase which is well bonded to the matrix (Fig. 5.3). *Crack deflections* a common effect in ceramic and metal matrix composites (Kelly and Denry, 2008; Scherrer et al, 1998; Mair et al, 1996), and it leads to a decrease of wear loss. *If the crack reaches an agglomerate (weaker zone), the propagation of the crack is accelerated (Fig. 5.7C).*

These observations are in good correlation with the specific wear rate (Fig. 5.5). The smoother surface of the wear track (Fig. 5.7C) noticed in the case of ZP samples was consistent with the results reported in the technical literature. As also mentioned by Kim et al. (Kim et al, 2012), the superior properties of zirconia (such as hardness, bending strength, fracture toughness and density) as compared to feldspathic porcelain, enabled it to maintain a smooth surface during the wear test.

It seems that the main strengthening mechanism, as observed in the fracture morphologic aspects after wear tests, is the strengthening effect of zirconia particles promoted by a strong bonding between feldspathic porcelain matrix and zirconia particles and by the load transfer mechanisms occurring from feldspathic porcelain matrix to the zirconia particles. Also, it should be mentioned that the zirconia agglomerates may have detrimental effect on the strengthening, and they are responsible for voids nucleation.

## 4. Conclusions

From the present investigation the following conclusions can be drawn:

- Both the feldspathic porcelain and the feldspathic porcelain composites reinforced zirconia agglomerates and by zirconia articles were successfully synthesized by heat pressing technique;
- the feldspathic porcelain composites reinforced by zirconia agglomerates (ZA) exhibited inappropriate wear response. This was explained by the destruction of the zirconia agglomerates during the mixture blending process, which resulted in sintering instabilities of the resultant material;
- the feldspathic porcelain composites reinforced by zirconia particles (ZP) showed the best wear response. This was attributed to the action of the uniformly distributed zirconia particles on the feldspathic porcelain matrix, which allowed the load transfer reinforcing mechanism to occur from the matrix to the reinforcement. Hence, it can be concluded that the ZP composite can be a good alternative to feldspathic porcelain especially when advanced wear properties are desired.

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## **CHAPTER VI**

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### **Tribological behavior of zirconia-reinforced feldspathic porcelain composites**

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#### **Abstract**

The purpose of this study was to characterize the wear behavior of dental feldspathic porcelain composites reinforced with different contents of zirconia particles. The tests were carried out using a ball-on-plate configuration, in artificial saliva at body temperature (37 °C). The zirconia particles were incorporated in different volume contents ranging from 10 up to 50%. *The results demonstrated* that zirconia plays a relevant role on wear behavior of zirconia reinforced feldspathic porcelain composites. The worn surfaces were characterized by field emission guns scanning electron microscope (FEGSEM). The results indicated that the addition of 10%, 20% or 30% (vol.%) zirconia into the dental feldspathic porcelain composites resulted in increased wear resistance combined with a lower coefficient of friction and a higher hardness. A decrease in wear resistance was recorded for higher zirconia contents, 40% or 50% (vol. %).

*Keywords:* wear; composite, dental restoration, glass-ceramic, zirconia.

## **1. Introduction**

During mastication, the restorative materials are subjected to sliding contact under normal and tangential loads. The friction and wear mechanisms occurring on dental restorative materials depend on different factors including environment (e.g. pH, oxygen, abrasive), loading and properties of the materials (Zhou and Zheng, 2008; Schuluetter et al 2012; Zheng et al, 2007; Mair et al, 1996). The degradation process of dental materials is also accelerated by substances from dietary and microbial metabolism (Souza et al, 2015).

Dental feldspathic porcelain are widely used to produce prosthetic restorative materials due to their good aesthetic, chemical inertness and biocompatibility (Strang et al, 1998). They are good choices, but it is well known that the main disadvantage of these materials is that they have poor mechanical properties such as low fracture toughness and tensile strength (Hamouda et al 2013; Stachowiak et al 2000; Manicone et al, 2007; Mitov et al, 2012; Song et al, 2008). Yttria-stabilized tetragonal zirconia polycrystal (3Y-TZP) has superior physical and mechanical properties (including high hardness, wear resistance, elastic modulus, and high melting temperature) than all ceramics (Hamouda et al, 2013; Stachowiak et al, 2000; SerkanSaridag et al, 2013). For instance, zirconia possesses a flexural strength ranging from 900 to 1200 MPa and the fracture toughness ranging from 9-20 MPa (Figueiredo-Pina et al, 2013).

There are several methods reported in technical literature to improve the properties (e.g. to prevent micro cracks) of the dental feldspathic porcelain composites such as framework support, dispersion strengthening, transformation toughening, residual surface stressing and surface treatment (Hamouda et al, 2013; Kasuga et al, 1992; Kasuga et al 1988; Shenoy and Shenoy, 2010; Usha et al, 2014, Maller et al 2012; O'Brien 2002; Atala and Gu, 2015). The incorporation of a high-strength biocompatible phase into feldspathic porcelain have been considered as potential alternative to overcome their main disadvantages (Hamouda et al, 2013; Kasuga et al, 1992; Kasuga et al, 1988; Ferraris et al, 1996; Verné et al, 1998; Verné et al, 1999; Verné et al, 2000).

To the authors knowledge, the studies regarding wear/mechanical behavior of zirconia reinforced feldspathic porcelain composites and produced by hot pressing process are scarce (Hamouda et al, 2013; Kim et al, 2012). As reported by Hamouda et al. (Hamouda et al, 2013) by adding 3 and 5 wt. % of Yttria partially stabilized zirconia to a

conventional dental feldspathic porcelain, it was observed an increase in flexural strength and fracture toughness as compared to the conventional dental feldspathic porcelain, while the Young modulus and hardness decreased. The variation of the mechanical properties with the amount of zirconia was also reported by Huang et al. (Huang et al, 2014). They studied the effects of zirconia content (from 0 to 30 wt.%) on microstructure and mechanical properties of zirconia-toughened lithium disilicate glass ceramic composites. In the case of the composites with small zirconia content (below 10 wt.%), zirconia acted as nucleation agent primarily and the microstructure was refined. On composites with larger zirconia content (from 15 to 30 wt. %), the zirconia particles restrained the phase separation of glass. The improvement on mechanical properties was attributed mainly to compressive stress reinforcement, phase transformation and bridging toughening mechanisms.

In order to simulate the masticatory motion different test configurations have been used, such as pin-on-disc (Preis et al, 2011), ball/pin-on-plate (Figueiredo-Pina et al, 2013), ball and crater (Antunes and Ramalho, 2003) etc. Concerning the environment, it plays an important role on tribology. The wear resistance of the tooth/restorative materials has been studied in electrolytes such as distilled water (Preis et al, 2011), artificial saliva or other acidic substance (e.g. citric acid). The artificial saliva can play both cooling and lubricant effect during wear process (Zhou and Zheng, 2008; Figueiredo-Pina et al, 2013; Li and Zhou, 2002).

The main aim of this study was to investigate the wear behavior of zirconia reinforced feldspathic porcelain with different zirconia (Y-TZP) particles contents ranging from 10 up to 50% (vol.%) in artificial saliva solution.

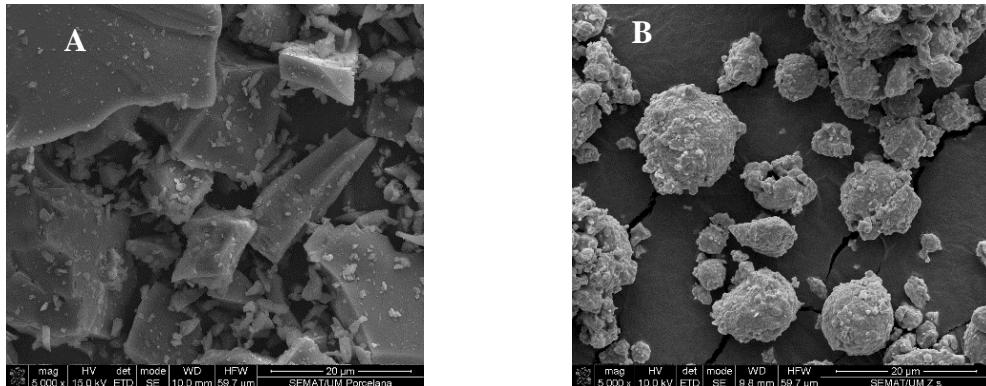
## 2. Experimental procedure

### 2.1. Materials

A dental glass-ceramic powder (Vita VM9, Vita, Germany) was used as matrix material. The chemical composition of the feldspathic porcelain is shown in Table 6.1. FEGSEM images of dental feldspathic porcelain powder (raw material) as provided by the supplier are shown in Figure 1A. The powder size distribution of feldspathic porcelain powder was  $D_{10}=2.49\text{ }\mu\text{m}$ ;  $D_{50}=18.92\text{ }\mu\text{m}$ ;  $D_{90}=50.71\text{ }\mu\text{m}$  and  $D_{ave}=23.47\text{ }\mu\text{m}$ .

**Table 6.1** Chemical composition of dental feldspathic porcelain powder (wt.%)

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	B <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	Other oxides
60-64	13-15	3-5	7-10	4-6	~2



**Fig. 6.1** FEGSEM images showing: A) Dental feldspathic porcelain powders and B) zirconia powders

Yttria-stabilized zirconia particles - 3Y-TZP (Innovnano, Portugal), were used as reinforcement (Table 6.2). FEG-SEM images of the pre-sintered zirconia powder are shown in Figure 6.1B. The powder size distribution of pre-sintered zirconia is D<sub>10</sub>=14.54 μm; D<sub>50</sub>=162.64 μm; D<sub>90</sub>=336.71 μm and D<sub>ave</sub>=166.44 μm.

**Table 6.2** Chemical composition of 3Y-TZP powder (wt.%)

ZrO <sub>2</sub> + HfO <sub>2</sub> + Y <sub>2</sub> O <sub>3</sub> + Al <sub>2</sub> O <sub>3</sub>	Y <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	HfO <sub>2</sub>	Other oxides
99.9	5.2±0.2	<0.4	<0.5	<0.5

## 2.2. Fabrication of zirconia reinforced glass-ceramic composites

The feldspathic porcelain was used as matrix material (named as Z0 from now on).

First, the 3Y-TZP powder provided by the supplier was sintered in a furnace at 1500°C for 2h. Afterwards, powder mixtures (feldspathic porcelain and sintered 3Y-TZP), were ball milled to reduce agglomeration and to enhance mixing, respectively. The dental feldspathic porcelain reinforced by 3Y-TZP was processed by the traditional heat pressing technique (Henriques et al, 2012; Henriques et al, 2011; Henriques et al 2014; Henriques et al 2011a; Henriques et al 2012b). Applied pressure was 7 MPa for 2 minutes at 970°C under vacuum (1 bar). *The 3Y-TZP content ratios in the mixture were selected as follows: 10%, 20%, 30%, 40 % and 50% (vol. %).* The samples are named according to the

volume content of zirconia (Z) in the feldspathic porcelain matrix, e.g. Z10 for 10% of zirconia, and so on.

### **2.3. Microstructural and chemical analysis**

The obtained samples were characterized in terms of microstructure, morphology and chemical composition by Field Emission Guns *Scanning Electron Microscopy (FEGSEM)* coupled to Energy Dispersive Spectrometer (EDS) (FEGSEM, FEI Nova 200, USA). The samples were sputter-coated with *carbon*.

### **2.4. Hardness measurements**

Vicker's microhardness measurements were performed on 10 different areas of the samples surfaces ( $n = 50$ ) using a microhardness tester (DuraScan, Emco-Test, Austria) with a load of 1 kgf during 15 s. Vickers hardness mean values were obtained as a average of 10 indentations per sample.

### **2.5. Wear tests**

Square test samples (10 x 10 x 2 mm) were embedded in epoxy resin. Samples were wet ground on SiC sandpapers down to 4000Mesh and then polished using diamond paste (1 $\mu$ m). Samples were ultrasonically cleaned in isopropyl alcohol for 15 min and then in distilled water for 15 min. A reciprocating ball-on-plate tribometer (Bruker-UMT-2) was used to evaluate the wear of square samples (10 x 10 x 2 mm) against Al<sub>2</sub>O<sub>3</sub> counterbody (10 mm diameter alumina ball, Goodfellow). The samples were placed in an acrylic electrochemical cell containing a Fusayama artificial saliva solution (Table 6.3), that was attached to the tribometer.

**Table 6.3** Composition of the stock Fusayama artificial saliva (Fusayama et al, 1963).

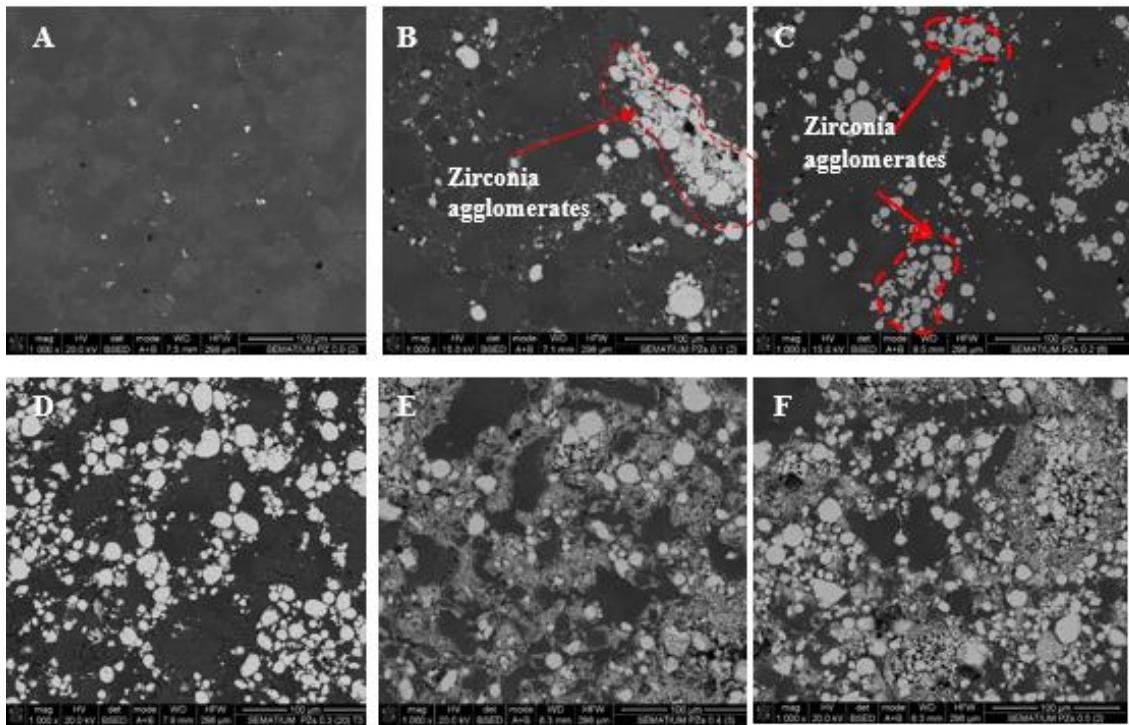
Compounds	g/L
NaCl	0.4
KCl	0.4
CaCl <sub>2</sub> · 2H <sub>2</sub> O	0.795
Na <sub>2</sub> S· 9H <sub>2</sub> O	0.005
NaH <sub>2</sub> PO <sub>4</sub> · 2H <sub>2</sub> O	0.69
Urea	1

The tribological parameters were 30 N normal load, at a frequency of 1Hz, and 3 mm of displacement, during 30 min. A set of five experiments was performed for each test condition. After testing, the specific wear rate was estimated by measuring the lateral width of the wear scars and using empirical mathematical equations assuming that the wear scars are formed by perfect ball geometry (Sampaio et al, 2015). All tests were performed in laboratory environment ( $20 \pm 2^\circ\text{C}$ ).

### 3. Results and discussion

#### 3.1. Microstructural characterization

FEGSEM images of the microstructure of feldspathic porcelain and feldspathic porcelain composites reinforced by zirconia particles in different content ratios (10%, 20%, 30%, 40% and 50%, vol. %) are shown in Fig. 6.2. It can be seen differences on the microstructure of the materials, with the white phase increasing with the increasing content of zirconia particles in the feldspathic porcelain matrix (dark phase).



**Fig. 6.2** Microstructure of the feldspathic porcelain and zirconia reinforced feldspathic porcelain composites: A) Z0; B) Z10; C) Z20; D) Z30; E) Z40 and F) Z50.

The chemical analysis of the sintered feldspathic porcelain reveals the presence of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ;  $\text{B}_2\text{O}_3$ ;  $\text{K}_2\text{O}$  and  $\text{Na}_2\text{O}$  (Fig 6.2A). Residual porosity can be seen in the micrograph represented by small black dots in the microstructure.

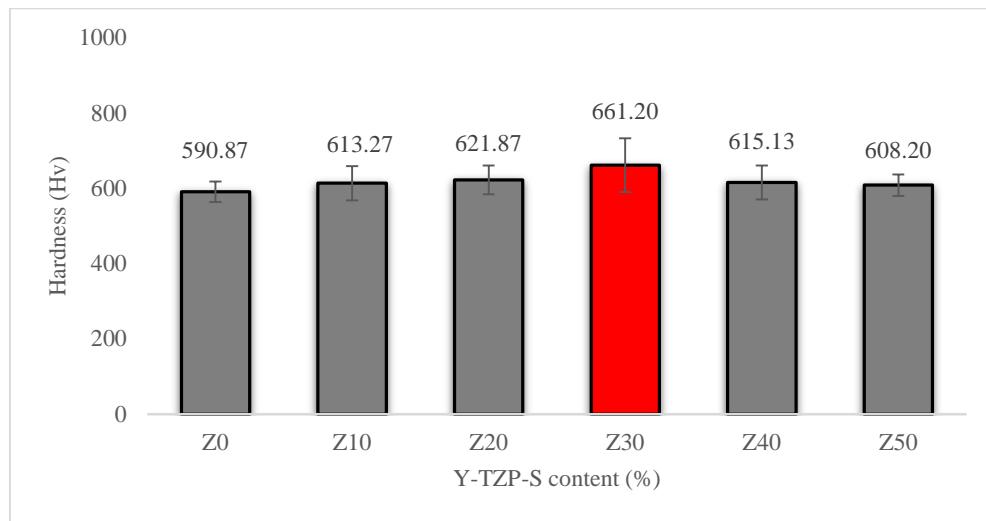
The microstructures of the dental feldspathic-porcelain-zirconia composites reinforced with zirconia particles are presented in Fig. 6.2B-F.

The micrographs show the coexistence of isolated zirconia particles and also of the zirconia agglomerates. It can be observed that by increasing the amount of zirconia particles from 10% to 30% (vol.%) there seems to be good bonding between the zirconia particles and feldspathic porcelain matrix and also a complet infiltration of the matrix inside de topografial details (asperities) of zirconia particles (Fig. 6.2 B-D).

It can be observed the segregation of the zirconia smaller powders to the grain boundaries of feldspathic porcelain, visible by the presence of grey phase (Fig. 2E and F) that increases with the volume content of zirconia in the composites (Z40-Z50). This had a negative influence on the sintering of the composites.

### 3.2. Hardness values

Fig. 6.3 shows the hardness results for all produced zirconia feldspathic porcelain composites as a function of zirconia particles content.



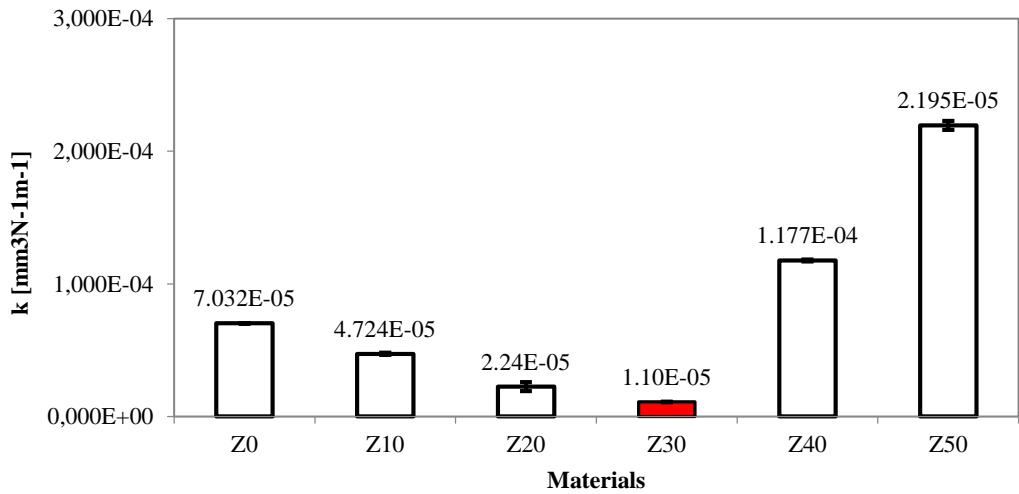
**Fig. 6.3** Hardness of the zirconia reinforced feldspathic porcelain composites as a function of the zirconia particles content.

The mean hardness values obtained for all produced zirconia reinforced feldspathic porcelain samples did not change significantly relative to the feldspathic porcelain samples ( $590 \text{ HV} \pm 3$ ). Nevertheless, it is seen a slight increase of the hardness values for samples with zirconia contents up to 30 vol.%. Greater zirconia contents lead to a slight decrease in the hardness values. The maximum hardness value was obtained for Z30 samples, being 12% higher than that of feldspathic porcelain.

This study is in agreement with the findings of other studies that reported no significant improvement on hardness values by the addition of partially stabilized zirconia to dental feldspathic porcelain (Hamouda et al, 2013; Gu et al, 2005).

### 3.3. Specific wear rate

*The specific wear rates for feldspathic porcelain and zirconia reinforced feldspathic porcelain as a function of Y-TZP-S content are shown in Fig. 6.4.*



**Fig. 6.4** Specific wear rates of the feldspathic porcelain and zirconia reinforced feldspathic porcelain composites as a function of the zirconia particles content.

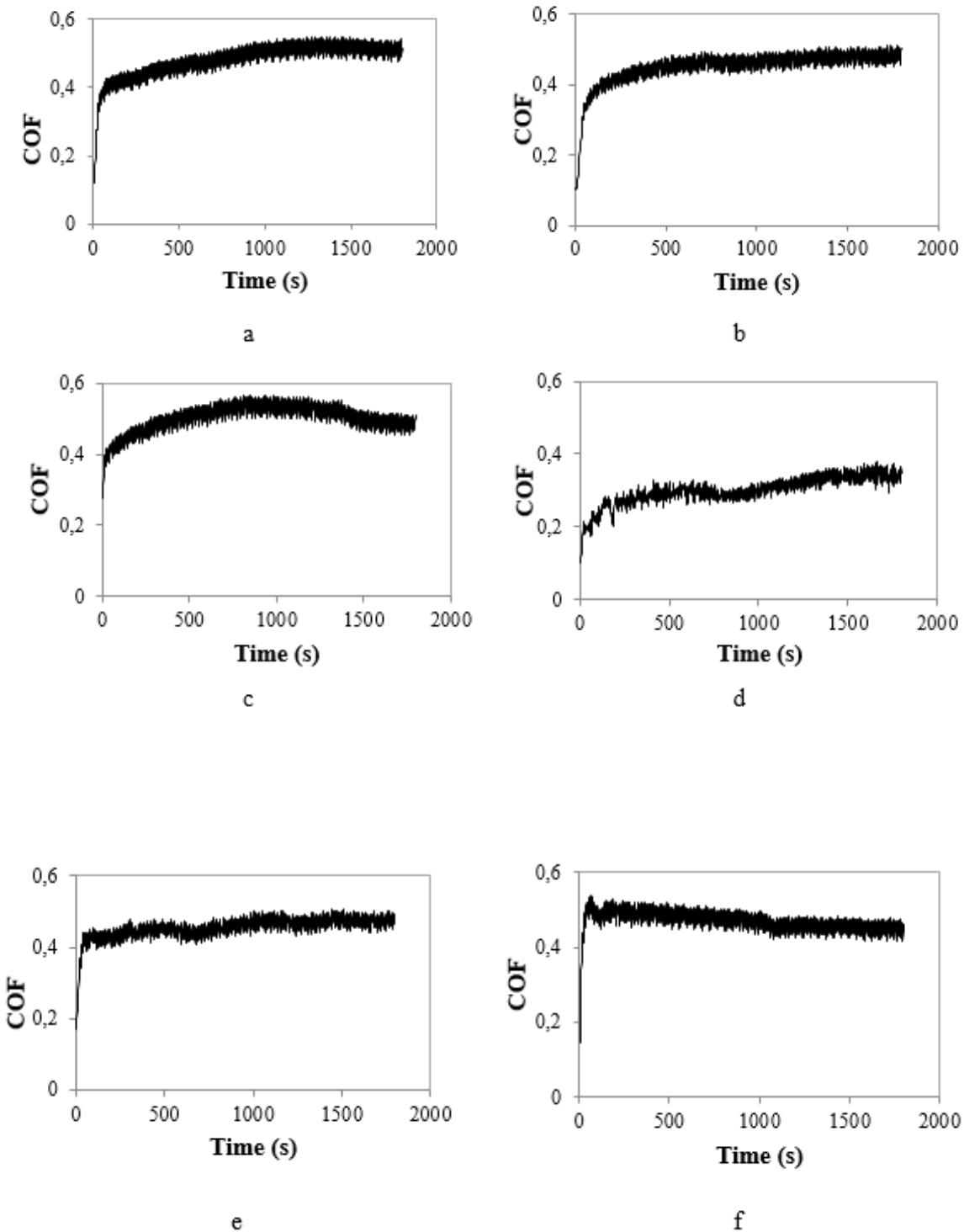
The wear performance was strongly influenced by the zirconia particles content. Corroborating the hardness results, the specific wear rates were significantly decreasing till the dental feldspathic porcelain composites reinforced by 30% of zirconia (Z30) as comparing to the feldspathic porcelain (Z0). In the case of the feldspathic porcelain composites reinforced by 40% and 50% (vol.%) of zirconia (Z40 and Z50) the specific wear rates were substantially increased as compared to MP and also to the other feldspathic porcelain composites (Z10, Z20 and Z30). The linear relation between wear volume of restorative materials and their hardness was also reported by Ramalho et al. (Ramalho and Antunes, 2005) and it has been also reported that these effect is more marked in tests carried out in an aqueous environment. In the presence of saliva the two contact materials can easily adhere at the microscopic level of sharp asperities (Yin et al, 2003).

### 3.4. Coefficient of friction

The evolution of the coefficient of friction (COF) during sliding for feldspathic porcelain and for feldspathic-porcelain-zirconia composites reinforced by different content ratios of zirconia against  $\text{Al}_2\text{O}_3$  ball in saliva artificial solution is shown in Fig. 6.5.

The COF value of the feldspathic porcelain and feldspathic-porcelain-zirconia composites attains the steady-state regime after a very short running-in period.

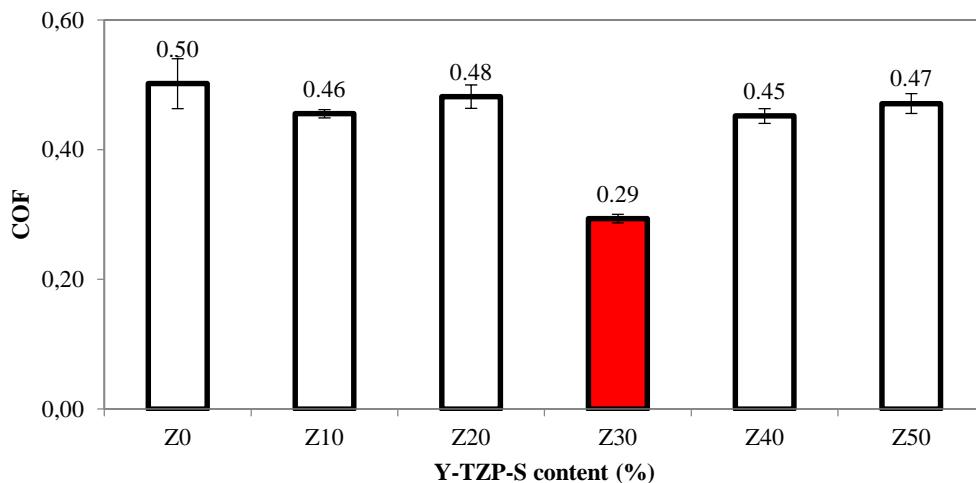
It can be observed that for higher zirconia contents, the COF values has a tendency to decrease at the end of the test, which may be due to the presence of a white “slurry” surrounding the wear track after the sliding test.



**Fig. 6.5** Evolution of COF with sliding distance for samples: a. Z0; b. Z10; c. Z20; d. Z30; e. Z40 and f. Z50.

In all studied cases, it can be observed higher oscillations of COF during the steady-state regime. It may be explained based on the transfer of the zirconia reinforced feldspathic porcelain composites samples material to the  $\text{Al}_2\text{O}_3$  ball (see fig. 6.5).

Fig. 6.6 presents the average COF (during the steady state regime) for dental feldspathic porcelain and all zirconia reinforced feldspathic porcelain composites. Concerning the COF mean values, a significant difference was found in case of 30 vol. % of zirconia as compared to other compositions studied. The COF measured for Z30 samples sliding against alumina in artificial saliva was significantly lower, down to 0.29, as compared to other studied cases (the COF was around 0.5).



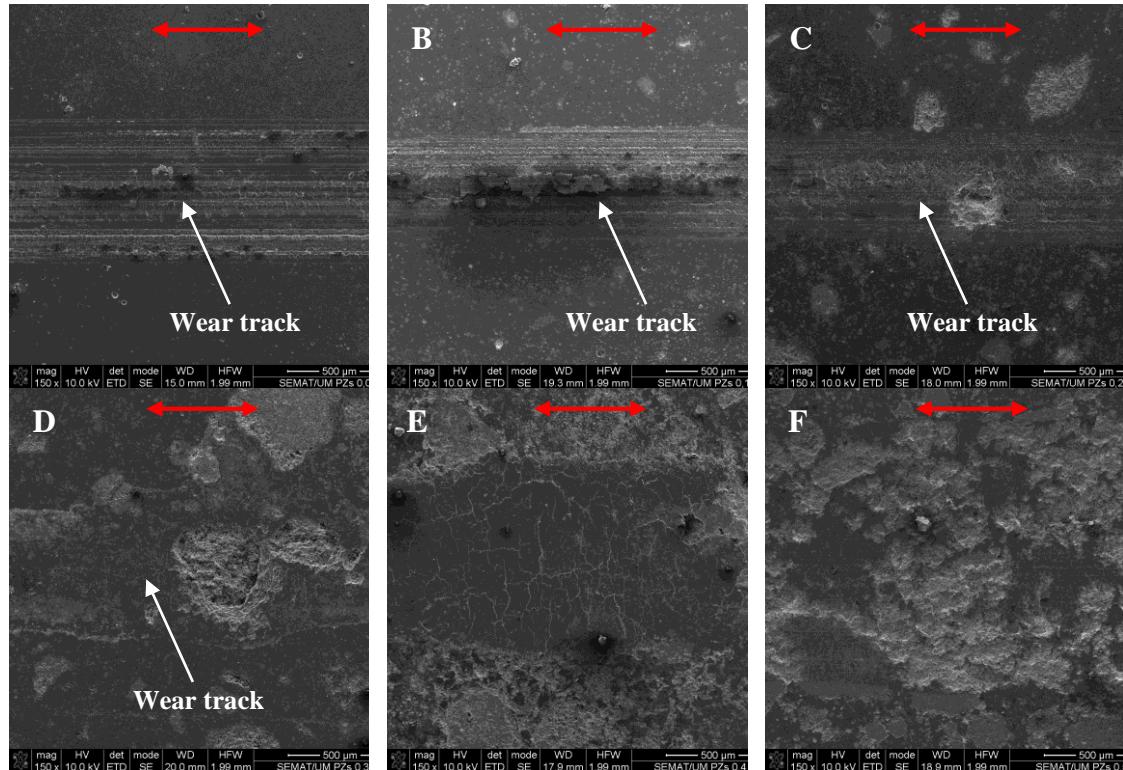
**Fig.6.6** COF of the glass-ceramic and zirconia reinforced feldspathic porcelain composites as a function of the zirconia content.

The COF value reported in literature for polished zirconia and veneer feldspathic porcelain is a higher value, around 0.55 (this tests were carried out also in artificial saliva, but the counter material was a natural teeth) (Wang et al, 2012). Also Yu et al. (Yu et al, 2006) in their study reported a similar COF value and the same evolution during the sliding test for feldspathic porcelain, using the same normal load ( $F_n=30$  N) and performed in artificial saliva.

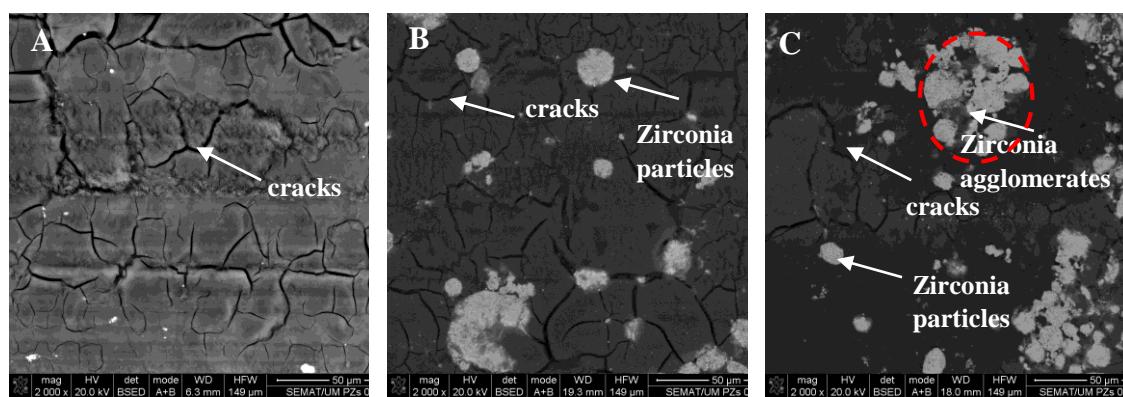
### 3.5. Microscopic analysis on worn surfaces

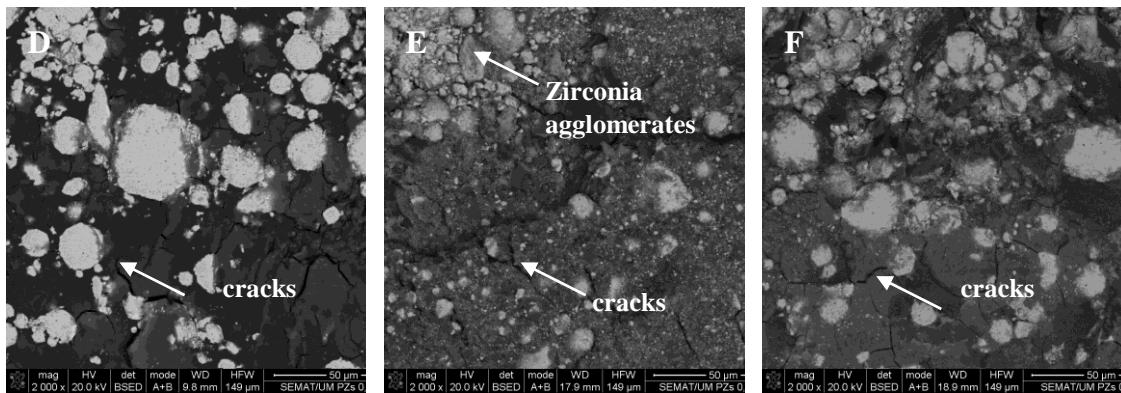
FEG-SEM images of the wear tracks after reciprocating sliding tests of both feldspathic porcelain and feldspathic-porcelain-zirconia composites against alumina immersed in artificial saliva are shown in Figs. 6.7, 6.8 and 6.9.

Fig. 6.7 shows the FEG-SEM images of the central area of the wear track (150x magnification), while Figs. 6.8 and 6.9 show the FEG-SEM images of the wear tracks with higher magnifications (2000x and 5000x). The sliding directions, are indicated by the arrows on the micrographs (Fig. 6.7).

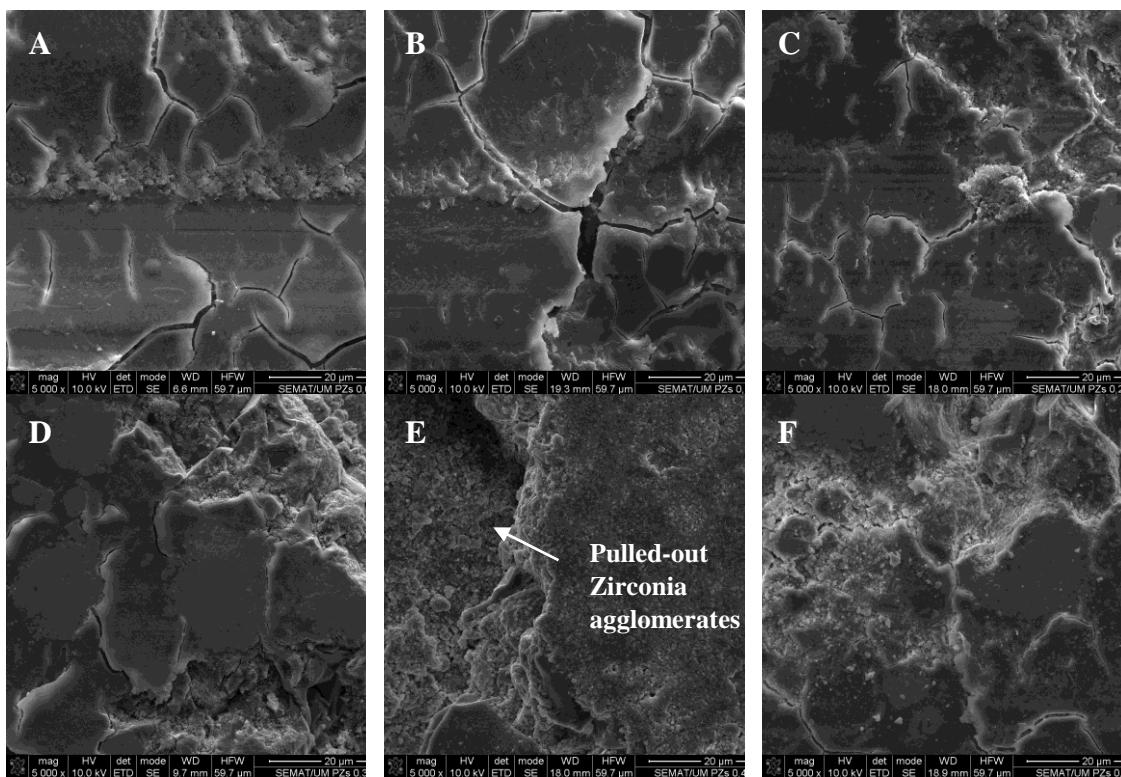


**Fig. 6.7** FEGSEM images of the midle area of the wear track: A) Z0; B). Z10; C) Z20; D) Z30; E) Z40 and F) Z50.



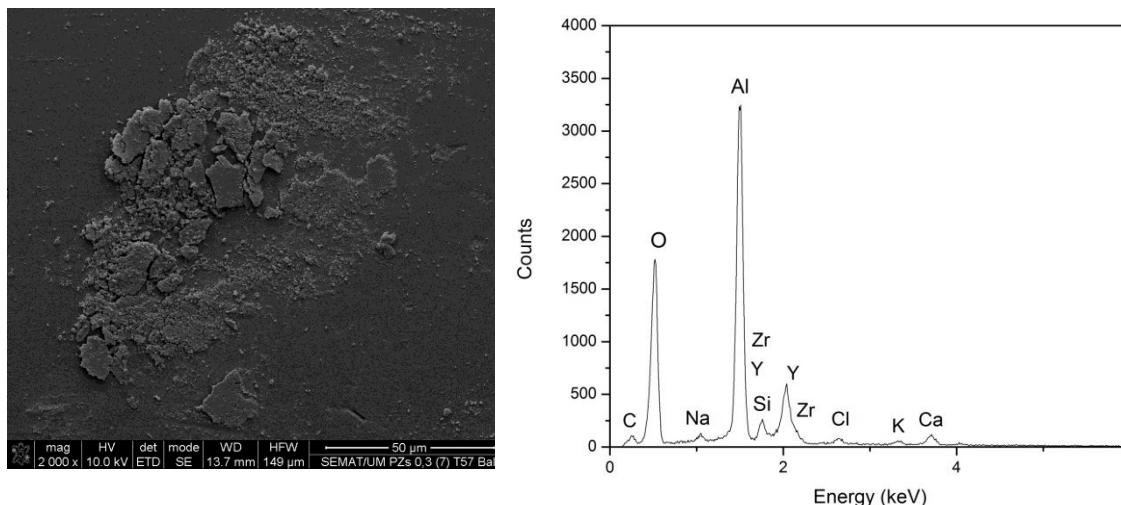


**Fig. 6.8** FEGSEM images of the wear track (2000x magnification A) Z0; B). Z10; C) Z20; D) Z30; E) Z40 and F) Z50.



**Fig. 6.9** FEGSEM images of the wear track (5000x magnification): A) Z0; B). Z10; C) Z20; D) Z30; E) Z40 and F) Z50.

FEGSEM images and EDS spectra of the counter material (alumina ball) surfaces after sliding against the test samples are shown in Fig. 6.10. EDS analysis revealed material transfer from the zirconia samples to the alumina ball, suggesting an adhesive wear mechanism. Also, EDS analysis revealed the presence of Al and O from the alumina ball as well as Zr, Y and Si coming from the zirconia reinforced feldspathic porcelain composites. The presence of C, Na, Cl, K, Ca can be attributed to the feldspathic porcelain and artificial saliva constituents.



**Fig. 6.10** SEM images of  $\text{Al}_2\text{O}_3$  ball after sliding against dental glass-ceramic composites reinforced by 30 vol. % of zirconia alloy and EDS spectrum.

Regarding the worn surface morphology of feldspathic porcelain and zirconia reinforced feldspathic porcelain composites reinforced by different volume fractions of zirconia particles, different wear mechanisms were noted by FEG-SEM analysis (Figs. 6.7, 6.8 and 6.9).

The sliding scratches can be observed on the feldspathic porcelain (Fig. 6.7A) and on the composites reinforced by 10% and 20% (vol.%) of zirconia (Z10 and Z20 – Fig. 7 B and C), being attributed to the abrasive wear caused by the transferred material to the ball (Fig. 6.10). The sliding grooves observed on the composites reinforced by 10% and 20% (vol.%) of zirconia (Fig. 6.7B and C) are less deep than the ones observed on the feldspathic porcelain surface (Fig. 6.7A).

The wear behavior of feldspathic porcelain is in accordance with the results presented in technical literature displaying rough surfaces with grooves, cracks, semicircular defects and chipping (Yu et al, 2006). It can be observed that in the case of the feldspathic porcelain composites reinforced by 30%, 40% and 50% (vol.%) of zirconia (Z30, Z40 and Z50 - Figs. 6.7 C,D and E) no wear grooves were observed.

Also, it can be noticed on SEM images (with a higher magnification) of the glass-ceramic (Figs. 6.8A and 6.9A) and of the feldspathic porcelain composites reinforced by 10% and 20% (vol.%) of zirconia (Z10, Z20) samples (Figs. 6.8 B and C and 6.9 B and C) multiples cracks through the wear tracks, that is a typical wear characteristic of the ceramics (as they are brittle and the wear of their surface occurs by fracture) (Oh et al, 2002). More cracks are observed in the case of feldspathic porcelain samples (Fig. 6.8A

and 6.9A). It can be seen that the number of cracks observed in the worn surface are decreasing with increasing zirconia content (Fig. 6.8 and 6.9).

The zirconia particles act as a second phase that is stiffer than the feldspathic porcelain matrix, allowing the load transfer reinforcing mechanism to occur from the matrix to the reinforcing phase. Regarding the feldspathic porcelain composites reinforced by 20 vol. % and 30 vol.% of zirconia (Z20 and Z30) it can be seen from the micrograph presented in Fig. 6.8C and D that the round zirconia particles are very well dispersed through the feldspathic porcelain matrix. There was a good bonding between the zirconia particles and the feldspathic porcelain matrix (Fig. 6.2) that may explained the increased extension of smooth surface noted on the worn surface from Z10 to Z30 samples (Figs. 6.7B, C and D) and as well as the lower number of cracks found and, consequently, the improvement on wear performance (Fig. 6.4).

The presence of some voids was detected on the worn surfaces of the Z20 and Z30 composite samples. These voids resulted mainly from the pull out of zirconia larger particles and particles agglomerates as seen in the backscattered FEGSEM images of the worn surfaces (Fig. 6.7 C and D). It is well known that the particles agglomerates are critic areas from the point of view of wear resistance and mechanical strength. It is important to point out that less cracks were observed on the worn surface of Z30 samples (Fig. 6.8D), as compared to the feldspathic porcelain (Fig. 6.8A) and also to the Z10 and Z20 samples (Fig. 6.8B and C). This is explained by the toughening effect produced by the dispersed zirconia particles in the feldspathic porcelain matrix. Hence, when a crack arises in the weaker matrix (feldspathic porcelain) it is deflected or blocked due to *the presence of a stronger zirconia phase which is well bonded to the matrix (Fig. 6.2)*. *Crack deflections* is a common effect in ceramic and metal matrix composites (Mair et al, 1996; Oh et al, 2002; Kelly and Denry, 2003), and it leads to a decrease of wear loss. *If the crack reaches an agglomerate (weaker zone), the propagation of the crack is accelerated (Fig. 6.9E)*. These observations are in good correlation with the specific wear rate (Fig. 6.4). The smoother surface of the wear track (Fig. 6.7D) noticed in the case of Z30 samples was consistent with the results reported in the technical literature. As also mentioned by Kim et al. (Kim et al, 2012), the superior properties of zirconia (such as hardness, bending strength, fracture toughness and density) as compared to feldspathic porcelain, enabled it to maintain a smooth surface during the wear test.

With the increase of zirconia content (Z40 and Z50) that have very large surface areas it is more difficult to disperse the zirconia particles uniformly in the glass-ceramic

matrix. It can be observed larger wear tracks area in the case of Z40 and Z50 composites (Fig. 6.7 E and F). It clearly showed that the surface damage was accelerated by reinforcing the feldspathic porcelain composite by a higher amount of zirconia. The SEM images of the Z40 and Z50 composites (Fig. 6.8 E and F and Fig. 6.9 E and F) present a lot of peaks and valleys (delamination). There are few regions with a smoother appearance aspect.

These smoother plateaus may correspond to some of the regions where the zirconia reinforcement bonded to the feldspathic porcelain matrix. The extensive rougher regions correspond to the regions where there is no bonding between the zirconia and feldspathic porcelain matrix. These rougher regions are areas of weakness from which failure was initiated to cause extensive wear of the composites reinforced by zirconia agglomerates. It can be observed from SEM images with a higher magnification (Fig. 6.8 E and F) that the grains/particles are fragmented. It is possible that fragments from the zirconia reinforced feldspathic porcelain composite contributed to the formation of the third body abrasive particles and consequently to an increase on volume loss.

These observations are in good correlation with the specific wear rate (Fig. 6.4).

It is well known that the degree of dispersion of reinforcement in a composite has an important role in wear resistance. Also, the agglomeration formation and second phase segregation are important factors in controlling the mechanical, wear and corrosion behavior (e.g. increasing stress concentrations at the grain boundaries, substantially accelerating the crack initiation and propagation etc.) of the composites.

It seems that the main strengthening mechanism, as observed in the fracture morphologic aspects after wear tests, is the strengthening effect of zirconia particles promoted by a strong bonding between feldspathic porcelain matrix and zirconia particles and by the load transfer mechanisms occurring from feldspathic porcelain matrix to the zirconia particles. Also, it should be mentioned that the zirconia agglomerates may have detrimental effect on the strengthening, and they are responsible for voids nucleation.

#### **4. Conclusions**

The main outcome of this work can be drawn as follows:

- The dental zirconia feldspathic porcelain reinforced composites were successfully synthesized by heat pressing technique;

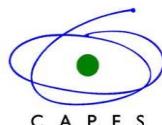
- *The results demonstrated* that the amount of zirconia plays a relevant role on wear behavior;

- The addition of 10%, 20% and 30% (vol.%) Yttria-stabilized zirconia particles in dental feldspathic porcelain resulted in a substantial improvement of the wear resistance, while the 40% and 50% (vol.%) contents had a detrimental effect on the wear resistance.

- Under saliva artificial at 37°C conditions against Al<sub>2</sub>O<sub>3</sub>, the optimal wear properties were obtained for the feldspathic porcelain reinforced with 30% (vol.%) of zirconia particles. The improvement on wear resistance was mainly attributed to the good dispersion of the reinforcement phase, which allowed the load transfer reinforcing mechanism to effectively occur from the matrix to the reinforcement.

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## **CHAPTER VII**

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### **Shear bond strength of veneering porcelain to zirconia: effect of surface treatment by CNC-milling and composite layer deposition on zirconia**

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## ABSTRACT

**Objectives:** The purpose of this study was to evaluate the shear bond strength of veneering porcelain to zirconia substrates modified by CNC-milling process or by coating zirconia with a composite interlayer.

**Methods:** Four types of zirconia-porcelain interface configurations were tested: RZ- porcelain bonded to rough zirconia substrate ( $n = 16$ ); PZ - porcelain bonded to zirconia substrate with surface holes ( $n=16$ ); RZI - application of a composite interlayer between the veneering porcelain and the rough zirconia substrate ( $n = 16$ ); PZI - application of a composite interlayer between the porcelain and the zirconia substrate treated by CNC-milling ( $n=16$ ). Surface holes on zirconia substrates were produced by CNC-milling machine. The composite interlayer was composed of zirconia-particles reinforced porcelain (30%, vol.%). The mechanical properties of the ceramic composite have been determined. The shear bond strength test was performed at 0.5 mm/min using a universal testing machine. The interfaces of fractured and untested specimens were examined by field emission guns scanning electron microscopy coupled to energy dispersive spectroscopy (FEG-SEM/EDS). Data was analyzed with Shapiro-Wilk test to test the assumption of normality. The one-way ANOVA followed by Tukey HSD multiple comparison test was used to compare shear bond strength results ( $\alpha=0.05$ ).

**Results:** The shear bond strength of PZ ( $100 \pm 15$  MPa) and RZI ( $96 \pm 11$  MPa) specimens were higher than that recorded for RZ (control group) specimens ( $89 \pm 15$  MPa), although not significantly ( $p>0.05$ ). The highest shear bond strength values were recorded for PZI specimens ( $138 \pm 19$  MPa), yielding a significant improvement of 55% relative to RZ specimens ( $p<0.05$ ).

**Significance:** This study shows that it is possible to highly enhance the zirconia-porcelain bond strength – even by ~55% - by combining surface holes in zirconia frameworks and the application of a proper ceramic composite interlayer.

**Keywords:** Zirconia; Porcelain; Shear bond strength, Composite interlayer, CNC-created surface holes

## 1. Introduction

Zirconia can be found within three crystalline forms: monolithic (m-t; 1173°C); tetragonal (t-c; 2370°C) and cubic (c-melting temperature; 2690°C). These transformations are reversible upon cooling with the tetragonal to monoclinic (t-m) transformation imparting compressive stresses to the material due to the occurrence of 4-5% volume expansion. Calcia (CaO), magnesia (MgO), ceria (CeO<sub>2</sub>), alumina (Al<sub>2</sub>O<sub>3</sub>) or yttria (Y<sub>2</sub>O<sub>3</sub>) are used as stabilizers of the tetragonal phase. The addition of 2-3 mol% Y<sub>2</sub>O<sub>3</sub> as stabilizing agent results in a fully tetragonal fine-grained zirconia ceramic material with 100% small metastable tetragonal grains (Y-TZP). Yttria stabilized tetragonal zirconia polycrystals (Y-TZP) has emerged as the most important ceramic for the fabrication of dental all-ceramic prostheses due to its high biocompatibility, chemical stability, aesthetics, outstanding flexural strength (up to 900-1200 MPa) and high fracture toughness (5.9-10 MPa m<sup>1/2</sup>) (Sevilla et al 2010; Kosmac et al 1999; Piconi and Maccauro, 1999; Denry and Kelly, 2008; Chevalier 2006).

Y-TZP is mainly used in the manufacturing of all-ceramic restorations as a substructure material which is veneered by feldspar-based porcelains to optimize the optical properties mimicking teeth structures. Despite the significant improvement on aesthetic outcome over the metal-ceramic restorations, the failure rate of dental all-ceramic restorations is high. Several studies have evaluated the clinical performance of zirconia-based restorations and reported high stability of zirconia frameworks (exceeding 97.8% over 5-years period). However, chipping and fracture of the veneering porcelain has been found, ranging from 6% up to 25% of the clinical cases over the same period of observation (Sailer et al, 2007; Tinschert et al, 2008). These failure percentage contrast with lower fracture prevalence on metal-ceramic restorations, which are reported to range from 8% up to 10% over 10 years (Creugers et al 1994, Scurria et al, 1998).

Hence, the most common form of all ceramic restorations failure is the delamination of the veneering porcelain. Such occurrence is considered to be a multifactorial phenomenon caused by the lack of proper framework support, microstructure defects, mismatch in thermal properties, occlusal overloads and poor mechanical interlocking of the porcelain (Dündar et al 2007; Kelly et al 1996).

This way, in order to reduce clinical failures of all ceramic restorations, considerable effort has been made in order to improve the bond strength between zirconia

and porcelain. Several factors affect the bond strength such as chemical bonds, mechanical interlocking, type and concentration of defects at the interface, wetting properties and the degree of compressive stress in the veneering layer (Fischer 2008; Kim et al, 2011). Different surface treatments of zirconia such as airborne-particle abrasion, application of a liner and creation of graded glass-zirconia structures has been proved to significantly improve the zirconia-porcelain bond strength (Aboushelib et al 2006, Kim et al 2011; Aboushelib et al 2008; Liu et al, 2015; Diniz et al, 2014).

In vitro and in-vivo fatigue studies have shown that failures of dental prostheses implies crack propagation towards the interface (Baldassari et al 2011; Bonfante et al 2009; Coelho et al 2009). The long-term success of the prosthesis is achieved if the crack formation could be eliminated or delayed. Thus, we hypothesized that the application of a composite interlayer on zirconia surfaces with well distributed holes prior to veneering porcelain could increase the mechanical strength of the interface enhancing the long-term success of the dental restoration. This approach has been shown to significantly enhance the bond strength in metal-ceramic restorative systems (Henriques et al 2011, Henriques et al 2012; Henriques et al 2012a).

The purpose of this study was to evaluate the shear bond strength of veneering porcelain to zirconia substrates modified by CNC-milling process or by coating zirconia with a composite interlayer.

## 2. Materials and Methods

### 2.1. Materials

In this study, a Y-TZP CAD/CAM blank (DD Bio ZW ISO, Dental Direkt GmbH, Spenge, Germany), Y-TZP powders (3YSZGSB, Innovnano, Portugal) and feldspar-based porcelain powders (VITA VM9, Bad Säckingen, Germany) were used. Commercial brand, chemical compositions, and manufacturer of each material are shown in Table 7.1. The size distribution of the porcelain and zirconia particles were the following: Porcelain:  $D_{10}=2.49\text{ }\mu\text{m}$ ;  $D_{50}=18.92\text{ }\mu\text{m}$ ;  $D_{90}=50.71\text{ }\mu\text{m}$  and  $D_{ave}=23.47\text{ }\mu\text{m}$ ; Zirconia:  $D_{10}=14.54\text{ }\mu\text{m}$ ;  $D_{50}=162.64\text{ }\mu\text{m}$ ;  $D_{90}=336.71\text{ }\mu\text{m}$  and  $D_{ave}=166.44\text{ }\mu\text{m}$ .

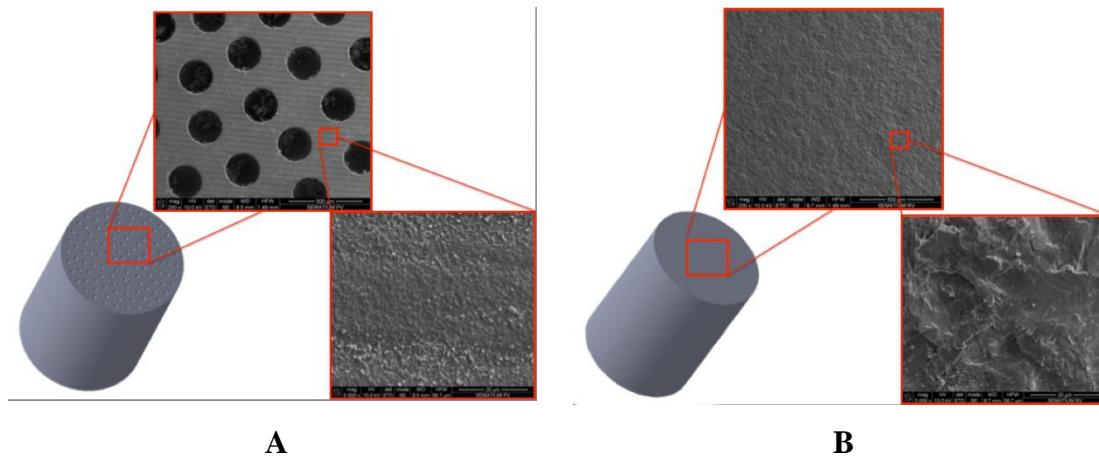
**Table 7.1.** Chemical composition and manufacturer of the materials used in this study.

Manufacturer/Brand	Chemical composition (Wt.%)	Material Type	Manufacturer
VITA VM9 Base Dentim –V9 Shade 3M2 (Lot n. 44670)	SiO <sub>2</sub> (60-64%), Al <sub>2</sub> O <sub>3</sub> (13-15%), K <sub>2</sub> O (7-10%), Na <sub>2</sub> O (4-6%), TiO <sub>2</sub> (<0,5%), CeO <sub>2</sub> (<0.5%), ZrO <sub>2</sub> (0-1%), CaO (1-2%), B <sub>2</sub> O <sub>3</sub> (3-5%), BaO (1-3%), SnO <sub>2</sub> (<0,5%), Mg, Fe and P oxides (<0,1%).	Feldspar-based porcelain	Vita Zahnfabrik, Bad Säckingen, Germany
3YSZGSB – Zirconia (Lot n. 1301PA046)	ZrO <sub>2</sub> + HfO <sub>2</sub> + Y <sub>2</sub> O <sub>3</sub> + Al <sub>2</sub> O <sub>3</sub> (3% mol Yttria) Y <sub>2</sub> O <sub>3</sub> (5,2±0,2) Al <sub>2</sub> O <sub>3</sub> (<0,4%)	Yttria-stabilized tetragonal zirconia polycrystals (Y-TZP)	Innovnano, Portugal
DD Bio ZW ISO CAD/CAM blank	ZrO <sub>2</sub> +HfO <sub>2</sub> +Y <sub>2</sub> O <sub>3</sub> >99% Al <sub>2</sub> O <sub>3</sub> <0,5% Other oxides <0,25%	Yttria-stabilized tetragonal zirconia polycrystals	Dental Direkt GmbH, Spenge, Germany

## 2.2. Specimens preparation

72 cylindrical (7.5mm in diameter and 5 mm in height) zirconia substrates were machined using a CNC milling machine (DWX 50, Roland, Japan) with spindle speed of 29000 rpm. The substructures were divided in two groups according to the type of surface treatment performed: A) CNC-miling treatment and B) grit-blasting. Homogeneous surface holes (group A) with 300 µm diameter and 400 µm depth were carried out using a Ø300 µm milling tool in a CNC milling machine according to a preset CAD pattern, as shown in Figure 7.1. The holes density was 6.6 holes per mm<sup>2</sup>. After this, all substrates were sintered in a furnace (ZircohnZhan, Germany) at 1500°C for 2 h. On the other hand, the production of rough substrates (group B) was performed by grit-blasting the surface of the sintered zirconia substrates with airbone-particles of alumina (Al<sub>2</sub>O<sub>3</sub>) with 110 µm diameter under 6 bar for 15 s and at a distance of 20-30 mm from the surface. The

sintering process produced a contraction (by 25%) of the substrates and the final dimensions of the cylinders were 6 mm in diameter and 4 mm in height. The surface holes of the substrates had final dimensions of 240 µm in diameter and 300 µm in depth. The specimens were rinsed in propyl alcohol for 5 min using an ultrasonic bath and dried at room temperature.



**Fig 7.1** Schematic of the cylindrical zirconia substrates and illustration of the two types of surface treatments performed: A) CNC-created surface holes; B) rough surfaces by grit-blasting.

Four types of veneering porcelain to zirconia interface configurations were tested in this study: RZ- porcelain bonded to rough zirconia substrate ( $n = 16$ ); PZ - porcelain bonded to zirconia substrate with surface holes ( $n = 16$ ); RZI - application of a composite interlayer between the porcelain and the rough zirconia substrate ( $n = 16$ ); PZI - application of a composite interlayer between the porcelain and the zirconia substrate with surface holes ( $n = 16$ ).

The composite used as interlayer was a mixture of porcelain and 30% (vol.%) of zirconia particles. The amount of porcelain powder in the mixture was selected based on other studies conducted by the authors that showed optimal mechanical properties of the composite with this composition. The zirconia powder was previously sintered at 1500°C for 2 h and deagglomerated before mixing to the porcelain powder. The powder mixture (feldspar-based porcelain and zirconia) was ball milled to reduce agglomeration and to enhance mixing. Porcelain was bonded to zirconia substrates by hot pressing in a graphite

die under vacuum (1.5 Bar) at 970°C (manufacturer recommendation for porcelain sintering temperature) and at a pressure of ~7 MPa (Fig. 7.1). That procedure was in accordance with that described by Henriques et al. (Henriques et al, 2012). The cavity of the graphite die was coated with a zirconia paint to prevent carbon contaminations. The heat rate was 65°C/min up to 970°C and then, after 2 min, the power of the induction heating furnace was shut down. The die cooled naturally at room temperature.

### **2.3. Mechanical tests**

The shear bond strength tests were carried out at room temperature and performed in a universal testing machine (Instron 8874, MA, USA), with a load cell of 25 kN capacity and under a crosshead speed of 0.5mm/s. Tests were performed in a custom-made stainless steel apparatus similar to that described by Henriques et al. (Henriques et al, 2012). The apparatus consisted in two sliding parts, each one with a hole perfectly aligned to the other. After aligning the holes, the specimens were inserted and loaded at the interface until fracture. The shear bond strength (MPa) was calculated by dividing the highest recorded load (N) by the cross sectional area of resistant porcelain ( $\text{mm}^2$ ).

The hardness mean values were calculated as an average of 10 indentations on the polished surface of each material ( $n = 5$ ). The indentations were made with a Vickers hardness indenter (EmcoTest-DuraScan, EMPRESA, PAIS) using a standard 136° pyramidal diamond ( $\text{HV}_1$ ), oriented perpendicular to the material surface.

The fracture toughness ( $K_{\text{IC}}$ ) of the specimens was determined by direct measurement of radial cracks generated by indentation on a load of 9.8 N. Measurements were performed after 24 h with minimal error of crack lengths due to continuing crack propagation in the presence of residual indentation stress (Blendell, 1979).

### **2.4. Analysis of the zirconia-porcelain interfaces and failure mode**

The zirconia-porcelain specimens from each group were randomly selected for microscopic analysis by field emission guns electron microscopy (FEG-SEM; NOVA 200 Nano SEM, FEI Company). For interface analysis, the specimens were embedded in self-curing resin, wet-ground using grit SiC sand-papers down to 4000 Mesh and polished with diamond paste (1  $\mu\text{m}$ ). After shear bond tests, the failure modes of the test specimens

were classified as: (1) adhesive, if no remnants of porcelain were found in the zirconia surface; (2) cohesive, if fractures occurred within the ceramic side; and (3) mixed, if porcelain remnants were found on the zirconia surface.

## 2.5. Statistical analysis

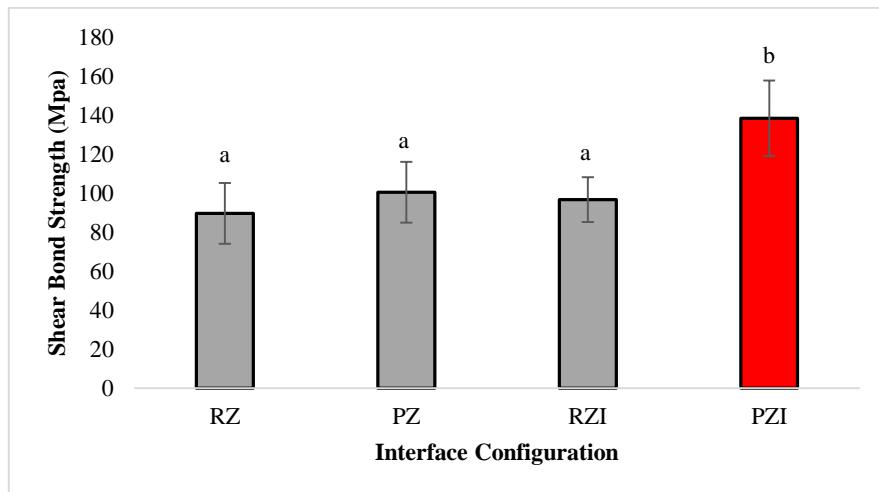
The results were analyzed using one-way ANOVA followed by Tukey HSD multiple comparison test. The Shapiro-Wilk test was first applied to test the assumption of normality. Differences between surface treatment and presence of interlayer in terms of shear bond strength were tested using t-test. P values lower than 0.05 were considered statistically significant.

## 2.6. Zirconia surface characterization

The average surface roughness ( $R_a$ ) of grit-blasted zirconia surfaces was measured using a profilometer (Mahr S5P, Germany). Two orthogonal measurements of 4 mm length were performed on the surface of each sample.

## 3. Results

Shear bond strength results recorded on porcelain to zirconia specimens with different interface designs are shown in Figure 2. The lowest shear bond strength values were recorded on the RZ (control group) specimens ( $89 \pm 15$  MPa) while the highest values were recorded on the PZI specimens ( $138 \pm 19$  MPa). The PZI specimens displayed a significant bond strength improvement of ~55% relative to the control group (RZ) ( $p<0.05$ ). The PZ ( $100 \pm 15$  MPa) and RZI ( $96 \pm 11$  MPa) specimens showed higher adhesion values than those recorded on RZ specimens, although not statistically significant ( $p>0.05$ ).



**Fig. 7.2.** Shear bond strength results for each type of zirconia-porcelain interface design: RZ - porcelain bonded to rough zirconia substrate; PZ - porcelain bonded to zirconia substrate with surface holes; RZI - application of a composite interlayer between the porcelain and the rough zirconia substrate; PZI - application of a composite interlayer between the porcelain and the zirconia substrate with surface holes. Same superscript letters indicate homogeneous groups (Tukey's test,  $\alpha=0.05$ ).

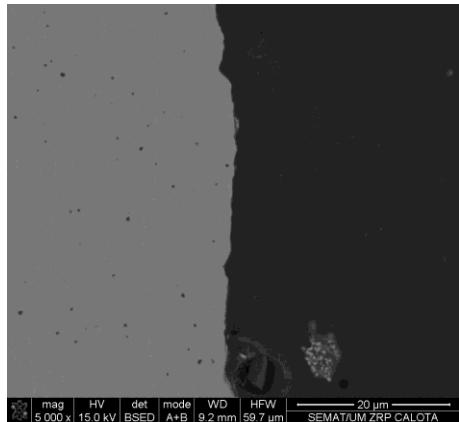
The mechanical properties of the base materials used in this study are shown in Table 7.2. It can be seen that the composite used as interlayer has improved mechanical properties relative to the feldspar-based porcelain, namely 2 times higher flexural strength and fracture toughness.

**Table 7.2.** Mechanical properties of the base materials used in this study.

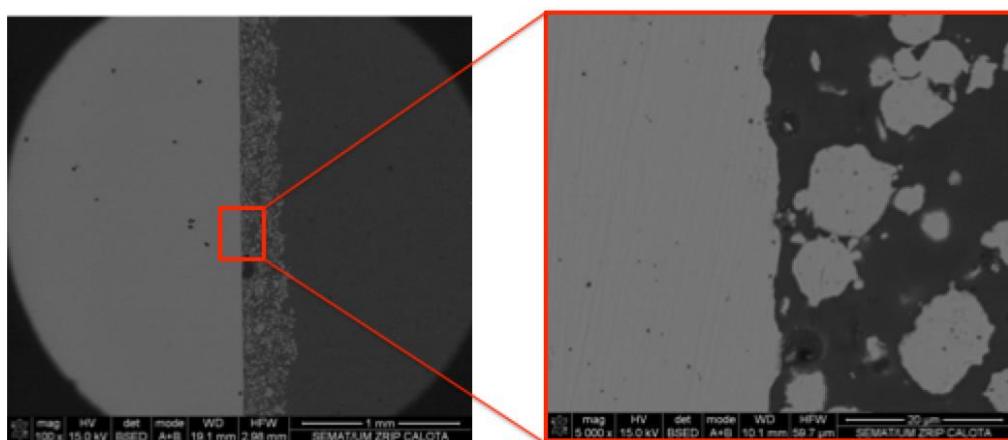
	Flexural Strength [MPa]	Fracture toughness [MPa·m <sup>1/2</sup> ]	Hardness [HV/GPa]
<b>Porcelain</b>	98±10	0.9	591/5.8
<b>Composite Interlayer</b>	218±24	2.1	661/6.5
<b>Zirconia (Y-TZP)*</b>	1200 ± (200)	>9	---
<b>* According to supplier</b>			

Micrographs of the porcelain to zirconia interfaces for the RZ specimens are shown in Figure 7.3. It is seen the profile roughness of the zirconia substrate produced by the grit-blasting treatment and an intimate contact between the two materials. Residual pores were detected in porcelain. The composite interlayer between the grit-blasted zirconia substrate and the veneering porcelain is shown in Figure 7.4. Zirconia particles were well

distributed within the porcelain matrix and a good adhesion was observed between the reinforcing phase and the matrix.

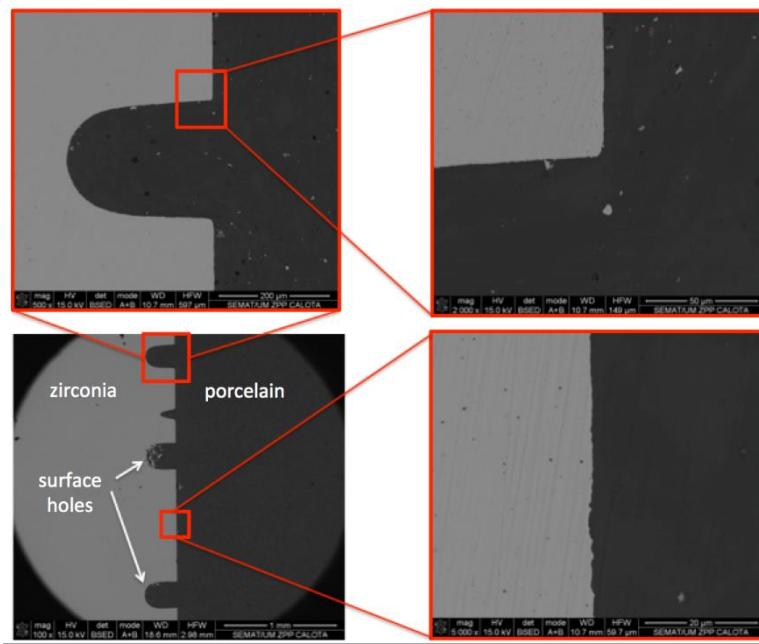


**Fig. 7.3.** FEG-SEM images of the veneering porcelain (dark phase) to zirconia (white phase) for RZ specimens.

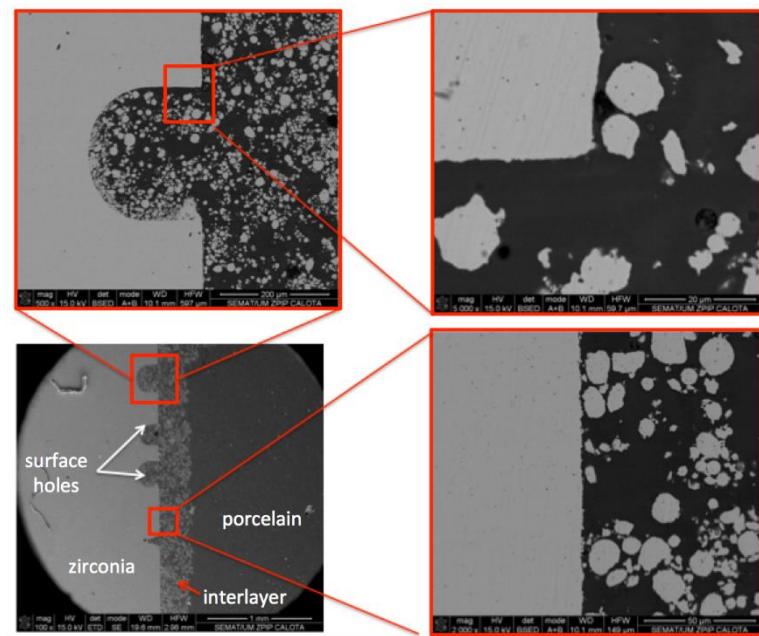


**Fig. 7.4.** FEG-SEM images showing the zirconia-interlayer-porcelain region of the RZI specimens.

The zirconia substrates with surface holes bonded directly to porcelain (PZI) and to a composite interlayer (PZI) are shown in Figures 7.5 and 7.6, respectively. It can be seen a good filling of the holes by the feldspar-based porcelain and by the composite interlayer, together with the absence of defects. Residual pores can be noticed.



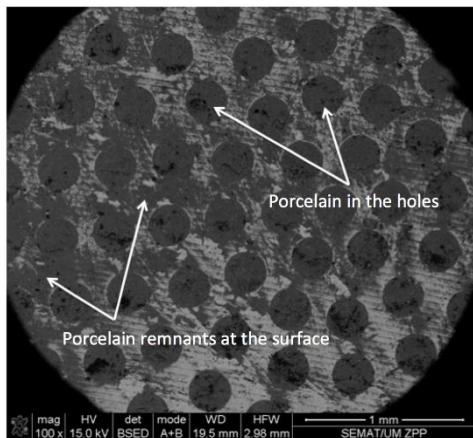
**Fig. 7.5.**FEG-SEM images of the veneering porcelain to zirconia inside and outside the holes region (PZ).



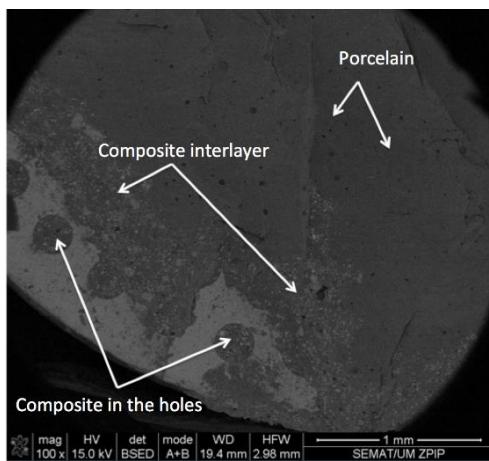
**Fig.7.6.** FEG-SEM images of the zirconia-composite interlayer interface inside and outside the holes region (PZI).

Specimens were classified under their failure types as adhesive, cohesive or mixed. It was though registered two types of failure: adhesive and mixed. An adhesive fracture was registered for 94% of the PZ specimens (Fig. 7.7). On the other hand, 56% of both RZ and RZI specimens, and 44% of the PZI specimens showed mixed fracture with

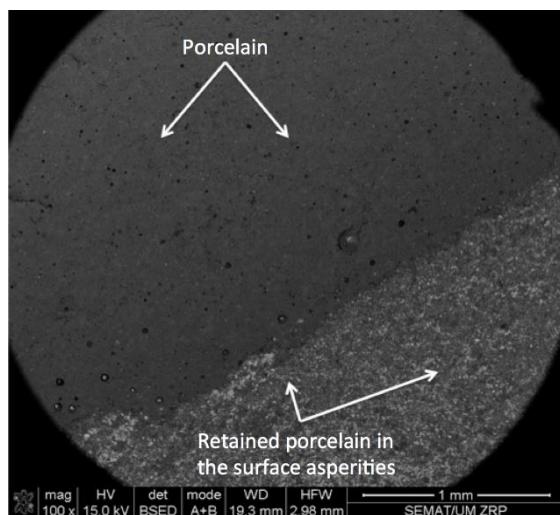
remnants of porcelain and interlayer being visible at the zirconia substrates (Fig.7.8 and Fig.7.9).



**Fig. 7.7** FEG-SEM images of the fracture surface of the zirconia substrates with surface holes (PZ).



**Fig. 7.8** FEG-SEM images of the fracture surface of the zirconia specimens with composite interlayer (PZI).



**Fig. 7.9** FEG-SEM images of the fracture surface of the sandblasted zirconia specimens (RZ).

#### **4. Discussion**

This study evaluated the influence of two different zirconia surface treatments and the application of a composite interlayer onto zirconia substrate on the shear bond strength of veneering porcelain to zirconia.

The surface holes at zirconia substrate (PZ) resulted in bond strength improvement relative to grit-blasted substrates (RZ), although not statistically significant. The RZ specimens, used as control group in this study, showed a starting high shear bond strength values due to the grit-blasted zirconia surface and the heat pressing of porcelain.

The air abrasion of zirconia substrates has been demonstrated to be the most applied surface treatment for bond strength improvement within the conventional methods (Kim et al, 2011; Yamaguchi et al 2012). Additionally, the heat pressing technique of porcelain to metallic or zirconia substrates have been shown to positively impact the porcelain cohesive properties and its adhesion to the substrate (Aboushelib et al, 2006; Aboushelib et al, 2008a). The porcelain used in this study has shown the highest shear bond strength value to grit-blasted zirconia substrates, in a comparison to other alternatives (Diniz et al, 2014). In fact, the bond strength values registered for RZ specimens are close to porcelain shear strength, evidencing the good adhesion between the two materials, and that the fracture could have occurred in the porcelain. This is supported by the significant amount of porcelain remnants retained at the zirconia asperities as seen at the fracture surface of RZ specimens (Fig. 7.9). On the other hand, few areas of porcelain remnants can be observed outside the PZ specimens surface holes (Fig. 7.7) due to the absence of surface treatment at that site.

The RZI substrates also showed a slight improvement in bond strength values relative to RZ specimens but, again, with no statistical significance. The presence of the composite interlayer, despite its better mechanical properties relative to feldspar-based porcelain (Table 2), did not contribute to significant increase in bond strength as reported in other studies on metal-ceramic adhesion (Henriques et al, 2012; Henriques et al, 2011; Henriques et al, 2012a). Henriques et al. reported a bond strength increase of ~140% when a metal/ceramic composite interlayer was used between a metallic substrate and the veneering porcelain (Henriques et al, 2012). They showed that the metallic particles of the composite interlayer bonded to the metallic substrate during the porcelain sintering, promoting additional mechanical interlocking between the substrate and the interlayer.

In the present study, as shown in Fig. 7.4 and Fig. 7.6, no diffusion bonding between the zirconia particles of the composite interlayer and the zirconia substrate was observed due to the high stability of zirconia at the porcelain sintering temperature (970°C).

The PZI specimens showed a significant improvement of bond strength relative to the other groups (RZ, RZI and PZ). They combined the effect of high mechanical interlocking promoted by the surface holes with the high strength and toughness of the composite interlayer, thus producing an optimized design of the zirconia-porcelain interface. Several studies have shown that for a crown or fixed partial denture to fail, a crack reaching the interface between the veneer and the core must occur (Baldassari et al, 2011; Coelho et al, 2009; Wang et al, 2013).

When cracks reach the zirconia-porcelain interface, they either grow along the interface or deflect into the porcelain. It was herein demonstrated that the introduction of a composite interlayer (with a fracture toughness that is twice of that of feldspar-based porcelain) at the interface between zirconia substrate and the veneering porcelain (group PZI) promotes a crack arrest mechanism that enhances the system's overall strength. This finding is in accordance with other studies that used a stronger ceramic phase to strengthen a typically weaker ceramic (e.g. glass or porcelain) or polymer (e.g. PMMA) (Verné et al, 2003; Asopa et al, 2015; Huang et al, 2014; Panyayong et al, 2002; Zuccari et al, 1997; Korkmaz et al, 2005).

The zirconia particles distributed in the porcelain matrix act as crack stoppers making more energy necessary for crack propagation. The fracture surface of PZI specimens showed that fracture occurred mainly within the porcelain, which means that cracks did not propagate within the interlayer or through the zirconia-interlayer interface. They were rather deflected to the interlayer-porcelain interface.

Another approach has been demonstrated to successfully prevent porcelain delamination in porcelain-fused-to-zirconia and consists in a functionally graded glass-zirconia material that is created by a glass-ceramic infiltration technique (Zhang et al, 2010; Chai et al, 2014; Grujicic et al, 1998. Liu et al. showed that the shear bond strength values of functionally graded glass-zirconia structures were significantly higher than those of conventional zirconia-porcelain sharp transition structures (Liu et al, 2015).

There are several ways to measure metal-ceramic bond strength. Within the most common mechanical tests are the shear bond test, the three-point-flexure test, the four-point-flexure test and the biaxial flexure test. The shear bond strength test results are

characterized for not being influenced by the Young's Modulus of the alloy as happens for bending tests (Hammad and Talic, 1996); by its relatively uniform distribution of interface stresses (Hammad and Stein, 1991) and by its suitability for evaluation of metal-ceramic and ceramic-ceramic bonds (Hammad and Talic, 1996; Anusavice et al, 1980).

Special attention must be paid to the device configuration because it can largely influence results. For instance, the shear device composed by a knife without a groove, generates high local stresses in the porcelain caused by small area of contact that can lead to the porcelain failure. Failure at the interface can be triggered by a cohesive failure in the porcelain and consequent propagation through the interface. The test device used in this study consisted on a piston-type shear device with half loop loading which reduces the stress concentration magnitude adjacent to the interface. This is considered an improved loading condition compared with concentrated force application at a single point (knife without a groove) or distributed only over a single layer (DeHoff et al, 1995).

Based on these facts, many authors used this test configuration in metal-ceramic bond strength characterization (Akova et al, 2008; Santos et al, 2006; Vásquez et al, 2009; Melo et al, 2005). This study presents shear bond strength mean values that are higher than those commonly reported for zirconia-porcelain systems in literature (Komine et al, 2012). The shear test device used can be in the origin of the values discrepancy. Ashkanani et al. showed similar bond strength values for zirconia-porcelain specimens using similar test protocol (Ashkanami et al, 2008). Nevertheless, more important than the absolute values stays the relative differences between the groups with the different variables.

## 5. Conclusions

From this study, the following conclusions can be drawn:

1. The addition of zirconia particles as reinforcing phase to porcelain resulted in significant improvement of mechanical properties (tensile strength, fracture toughness and hardness) relative to feldspar-based porcelain;
2. The surface holes (PZ) and the application of composite interlayers (RZI) on zirconia produced separately an improvement of zirconia-porcelain bond strength

- values relative to conventional zirconia-porcelain specimens (RZ), although not statistically significant ( $p>0.05$ );
3. Holes produced by CNC-milling coupled with the composite interlayer produced a significant bond strength improvement (by ~55%) relative to conventional zirconia-porcelain specimens (RZ).

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## **CHAPTER VIII**

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### **General Discussion**

In order to improve the mechanical performance of the all-ceramic substructures for dental restorations, it is critical to understand the procedures used to fabricate these materials. From there, were evaluated the best conditions for optimization of these substructures.

This thesis is devoted to the mechanical and microstructural study of the feldspathic porcelain-zirconia composites for dental applications. In this thesis was studied the influence of the several variables: Previous characterization and comparative study between zirconia commercial and zirconia synthesized by CPM; the type of zirconia particles (particles and agglomerates) in glass-ceramic matrix; the mechanical performance from the zirconia content (0-50% vol.%) in feldspathic porcelain matrix, the wear behavior for all composites; and the adhesion/interaction between porcelain-zirconia substructures with different surface treatment. Next, a general discussion about each of these topics is presented, focusing on the main highlights of each theme.

#### **8.2 Commercial zirconia vs. synthesized zirconia**

In this thesis was firstly studied the characteristics of the commercial zirconia and synthesized zirconia using different Yttria contents (3, 4 and 5 mol.%) by Complex Polymerization Method. This study had high importance in this thesis from the correct choice of the obtaining method for zirconia particles in all-ceramic substructures, in other words, enabled to explain the “*Why?*” of this selection. The effect of calcination temperature (800 to 1000 °C) was assessed to zirconia obtained by CPM and indicates that the increase in calcination temperature and time, induce variations in intensity and width of peaks (Fig 2.1). Besides, the increase of the crystallite size (11.5 to 27.9 nm) may occur due the major atomic diffusion at high calcination temperature, increasing the structural packing that enhanced consequently the crystallite size (Davar et al, 2013; Grzebielucka et al, 2010). Comparing the results between zirconia synthesized and

commercial (27.9 and 37.0 nm) an increase of 32%, this behavior can be explained from the different manufacturing method employed, CPM and high energy milling, respectively. Related to yttria content, the increase of dopant content (3,4 and 5 mol. %) into crystal lattice promote the decrease in crystallite size for the same temperatures and distinct compositions (Chevalier et al, 2009). In terms of unit cell volume, the increase of dopant content may decrease the tetragonal phase and tends to change to cubic phase (major values of unit cell volume) (Silva et al, 2010). In this case, the thesis emphasis will be placed on the minor stabilizing contribution of the dopant cations, whereas, in tetragonal phase production. The thermoanalysis presented the behavior of the specimens from the decomposition progress in several steps and is based on a thermally induced anionic redox reaction (Laberty-Robert et al, 2001). The materials evaluated are thermally stable at 1100 °C and the weight loss for synthesized specimens with yttria content (3, 4 and 5 mol%) is major than compared as commercial zirconia, 85, 72, 86 and 2%, respectively (Fig 2.6). The large weight loss present in specimens synthesized by CPM can be explained from the volatilization of the organic compounds (CO, CO<sub>2</sub>, H<sub>2</sub>, N and N<sub>2</sub>), during combustion reaction, decomposition of nitrates and material crystallization, unlike what happens with commercial zirconia obtained by high-energy milling. The Raman spectroscopy was used in this thesis to confirm the presence of tetragonal phase of synthesized materials from the changes in the zirconia bond angles and lengths (Casellas et al, 2001; Ishigame and Sakurai, 1977; Bouvier et al, 2001; Ramos et al 2013). The different calcination temperature and dopant content probably caused few spectral variations at the tetragonal and cubic phases (260, 464 and 642 cm<sup>-1</sup>) (Casellas et al, 2001). The results indicate that the CPM is a good technique to produce monophasic zirconia with different Yttria contents. However, independent of calcination temperature and Yttria content used, the results not exceeded the commercial zirconia. In this context, the use of the commercial zirconia is endorsed for dental applications.

### ***8.3 Zirconia particle effect in feldspathic porcelain matrix***

One of the aims of this thesis was to evaluate the influence of the type of zirconia reinforcement. The use of reinforcement is widely used to improve the mechanical properties of the dental materials, composites especially. Thus, this study was developed in order to maximize the mechanical performance of these composites. Were used two

types of particles: (yttria-stabilized zirconia 3Y-TZP agglomerates (ZA) and pre-sintered yttria-stabilized zirconia (3Y-TZP) particles (ZP) inserted in feldspathic porcelain matrix to produce the composites by Hot pressing technique. The results indicates that composites present different microstructures related to the type of the zirconia reinforcement used. To (ZA), the agglomerates are not visible in feldspathic porcelain matrix, this behavior can be confirmed due to the weakly bond within the agglomerates, they are easily destroyed during the mixing procedure. This produced a fragmentation of the powders in micrometric and nanometric powders that covered the porcelain powders and negatively impacted the sintering and densification of the composites, reducing dramatically the strength of the composite (Fig. 3.3). Most of the porcelain powders were covered by fine zirconia particles that sinters at 1500 °C and not 970 °C as happens with glass-ceramic. To improve the mechanical strength of the zirconia agglomerates (ZA), these agglomerates can be ball-milled with steering suspension of the mixture in alcohol until complete evaporation. The mechanism was explained by the infiltration of the feldspathic porcelain phase into the zirconia agglomerates, leading to a partial spreading of each particle into agglomerates of small zirconia grains (about 1 mm size) (Verné et al, 2003). On the other hand, the improvement in flexural strength of the composite (ZP) compared as Z0 (monolithic porcelain) is explained by the action of the uniformly distributed dense zirconia particles (pre-sintered agglomerates). The zirconia particles act as a second phase that is more rigid than the porcelain matrix, allowing the load transfer reinforcing mechanism to occur from matrix to the reinforcing phase. It is possible to see round zirconia particles spread through the porcelain matrix few pores can be detected within the porcelain matrix of feldspathic porcelain/zirconia-porcelain samples and they are preferentially located at the vicinities of the ZPs rather than in the feldspathic porcelain matrix. The results in Fig. 3.4 and 3.5, show clear differences between the composites in flexural strength and hardness to according as type of reinforcing phase used. The (ZA) present lower flexural strength and hardness (29.7 MPa and 254.67 Hv), when compared as Z0 (glass-ceramic) and (ZP), respectively. Composites hot pressed with pre-sintered zirconia (3Y-TZP) particles (ZP) in feldspathic porcelain matrix showed significantly higher hardness than reinforced composites with (ZA). These results are based in a good dispersion and good bonding between the reinforcing zirconia phase and the feldspathic porcelain matrix (Fig 3.3). Besides the improvement noticed in flexural strength of the (ZP) it is also expected an improvement in the toughness behavior relative to pure porcelain (Verné et al, 2003). The toughening mechanism is based on the crack

deflection around the zirconia particles. In all composites, it is possible to see the presence of pores remnants the porosity found in cast and pressed substrates were less %. Thus, these results indicate that the zirconia particles (ZP) present higher mechanical properties can be widely used as ceramic reinforcement.

**8.4 Zirconia content effect in mechanical performance of the composites feldspathic porcelain-zirconia** In this study was investigated the mechanical properties of the feldspathic porcelain-zirconia composites. Porcelain has been for long time the veneering material of choice used in metal-ceramic and all-ceramic dental restorations. However, it lacks in mechanical strength when compared to the underlying materials and therefore its mechanical properties could be desirably improved. Thus, the addition of zirconia particles to porcelain affected significantly the properties of these base materials, increasing fracture strength, hardness and toughness (Huang et al, 2014; Verné et al 2003; Assopa et al, 2015; Panyayong et al, 2002; Zuccari et al 1997; Rorkmaz et al 2005). The composites were prepared according the particulate composites theory and Voigt & Reuss mixing rule, when the particulate reinforced composites usually contain less reinforcement (up to 40 to 50 volume percent) due to processing difficulties and brittleness (Campbell, 2010). In this work, were incorporating different volume fractions (0-50% vol.%) of zirconia particles (3Y-TZP) in a porcelain matrix obtained by Hot pressing that allows to minimize the defects such pores and flaws in the specimens (Henriques et al, 2014; Henriques et al 2011; Henriques et al 2012). The pre-sintering of the zirconia agglomerates supplied by the manufactures intended to produce larger and dense particles that could be used as reinforcing phase. The microstructure analyses revealed a well distribution of zirconia particles although zirconia agglomerates and residual pores were found in the microstructure of all specimens. The segregation of the zirconia smaller particles to the grain boundaries of feldspathic porcelain was noted by the presence of a white phase that increases with the volume content of zirconia in the composite (Z10-Z50) (Fig. 4.2). Both zirconia agglomerates and small pores, produced by entrapped air during porcelain fusing, were considered flaws. In this context, the preparation of powders is crucial for achieving composites with high strength and, for future interactions. The best properties were obtained to composites with 30% (vol.%) of zirconia reinforcing phase in flexural strength ( $218\pm24$  MPa) and fracture toughness ( $2.1\pm0.9$  MPa  $m^{1/2}$ ). This results can be explained from the significant load transfer

strengthening requires that the Young's modulus of the reinforcing phase should be at least twice of that of the matrix as well as by the proper bonding between the two phases. The fracture toughness,  $K_{IC}$ , increased with the zirconia content. The hardness (HV/GPa) Table 3.3 had a steady increase of the hardness values with the increasing content of zirconia phase up to 30% (vol.%) – Z30 and decrease with the increase of the zirconia content for groups Z40 and Z50. The flexural strength and fracture toughness were increased by >100%, and hardness by 12% relative to feldspathic porcelain values. Thus, the improvements seen in the zirconia-reinforced feldspathic porcelain can constitute a promising alternative to current feldspathic porcelain in the manufacturing of dental restorations, especially in posterior teeth.

### ***8.5 Wear effect according the type of zirconia particles applied***

The influence of type zirconia particles on the wear behavior for porcelain-zirconia composites was assessed in this thesis. The wear tests were performed with two types of particles {Yttria-stabilized zirconia ( $ZrO_2$ -3%  $Y_2O_3$ ) agglomerates (ZA) and pre-sintered Yttria-Stabilized Zirconia ( $ZrO_2$ -3%  $Y_2O_3$ ) (ZP)}. The results revealed an improvement on wear behavior for dental composites reinforced by (ZP) when compared as glass-ceramic (Z0) and (ZA). This improvement on wear resistance of the composite reinforced by zirconia particles is attributed to the effect of reinforcement (improving the grain-boundary strength) by the action of the uniformly distributed pre-sintered zirconia particles, which allows the load transfer reinforcing mechanism to occur from the matrix to the reinforcement Sug Won Kima et al (2003). The results of hardness (Fig. 5.4) may be considered the main material parameter governing its wear behavior (Hutchings, 1992). The increase in hardness with the addition of the sintered zirconia particles may eventually be explained based on the fact that the ZP placed at the grain interfaces of dental porcelain, create barriers to slip thus increasing strain hardening during plastic deformation (strengthening effects of sintered zirconia particles), and consequently an improvement on wear performance. The hardness values of glass or ceramic decreases in an aqueous environment. In the presence of saliva the two contact materials can easily adhere at the microscopic level of sharp asperities (Yin et al 2003; Monasky and Taylor, 1971) The evolution of the coefficient of friction (COF) (Fig. 5.6) can be explained based on the fact that as there is not bond between the feldspathic porcelain and zirconia

agglomerates (zirconia powders that covered the porcelain powders), the zirconia powders were released into the contact. It was observed white “slurry” around the contact zone during the sliding test, so the zirconia powder that covered the porcelain powders was mixed with the saliva. In feldspathic porcelain samples (Fig. 5.7a and 5.8b), the sliding grooves being attributed to the abrasive wear (caused by the asperities of the alumina ball – of the transferred materials to the ball). Also, it can be noticed multiples cracks through the wear track (typical characteristic of the ceramics) (Oh et al, 2002). The feldspathic porcelain has a small amount of zirconia beside abrasive wear and micro cracking, also crack deflection can be observed (Fig. 5.8a3). However, to composite reinforced by zirconia agglomerates was possible to see a largest wear track (Fig. 5.7b). In Z0/ZA composites is not being visible any the zirconia agglomerates (Fig. 5.2). This suggests that they were destroyed during the mixing procedure as previously mentioned in “*Zirconia particle effect in porcelain matrix*”. To (ZP) composites have a stronger bonding between feldspathic porcelain matrix and zirconia particles and the effect of the zirconia’s reinforcement on the matrix most probably due to restrictions on matrix slip (mainly in the zones where the zirconia particles are well dispersed). The zirconia powders revealed a beneficial effect on the decrease of the wear resistance as compared with both the feldspathic porcelain and also with the composites reinforced by zirconia agglomerates (Z0/ZA). Therefore, dental feldspathic porcelain composite reinforced by zirconia particles showed the best wear response. It can be concluded that composite reinforced by zirconia particles can be used a restorative material, and seems to be a better choice than the feldspathic porcelain, as it showed a less wear.

### **8.6 Wear effect according the zirconia content in porcelain matrix**

The results presented in this study shown the wear characterization of Dental Porcelain reinforced by Yttria-Stabilized Zirconia *against alumina*. The tests were carried out using a ball-on-plate configuration, in artificial saliva at body temperature ( $37 \pm 2^\circ\text{C}$ ). The wear resistance is investigated *as a function of zirconia content*. The zirconia was incorporated in 10, 20, 30, 40 and 50 percent by volume to dental porcelain. *The results demonstrated* that zirconia plays a relevant role on wear behavior of dental based-composites. The results indicated that the addition of 10, 20 and 30 vol. % yttria stabilized zirconia to the dental porcelain resulted substantially improving the wear resistance (Fig. 6.4) combined with a lower coefficient of friction (COF) (Fig. 6.6) and a higher hardness

(Fig. 6.3), while by increasing more zirconia content (40 and 50 vol. %), a drop on wear properties was observed. These results can be explained due to the strengthening of the grain boundaries and to the good dispersion of the reinforcement, which allows the load transfer reinforcing mechanism to occur from the matrix to the reinforcement. In all studied cases, the coefficient of friction (COF) revealed higher oscillations during the steady-state regime. It may be explained based on the transfer of the dental porcelain composites to the  $\text{Al}_2\text{O}_3$  ball (Fig. 6.10). The COF for feldspathic porcelain-zirconia composites was similar to the results reported in literature (Wang et al, 2012) Also Yu et al. (Yu et al, 2006) when used the natural teeth and 30N of load. Under saliva artificial at 37°C conditions against  $\text{Al}_2\text{O}_3$ , the optimal wear properties were obtained in the case of the addition of 30 vol. % of zirconia the dental porcelain composite. The hardness values obtained for all produced dental composites reinforced by 3Y-TZP were higher than the glass ceramic samples ( $590 \text{ HV} \pm 3$ ). The maximum hardness value was obtained for the dental feldspathic porcelain composite reinforced with 30 vol. % of 3Y-TZP (increases with 12% as compared to the feldspathic porcelain). As reported by several studies (Hamouda et al, 2013; Gu et al, 2005) no improvement on hardness values was observed by the addition of partially stabilized zirconia to dental feldspathic porcelain. Corroborating the hardness results, the specific wear rates were significantly decreasing till the dental porcelain reinforced by 30 vol. % 3Y-TZP as comparing to Z0. In the case of the composites reinforced by 40 and 50 vol. % 3Y-TZP the specific wear rates were substantially increased as compared to Z0 and also to the other composites (Z10, Z20 and Z30). The linear relation between the wear volume of restorative materials and their hardness was also reported by Ramalho et al (2005) and it was reported that these effect is more marked in tests with saliva. As mentioned also by Huang et al (2014) as compared to feldspathic porcelain, the superior properties of zirconia (such as hardness, bending strength, fracture toughness and density) enabled it to maintain a smooth surface during the wear test. Thus, the stronger bonding between feldspathic porcelain matrix and zirconia particles (30% vol.%) guarantee the highest mechanical properties and can be applied in all-ceramic restorations.

## **8.7 Surface treatment and adhesion**

This study evaluated the influence of different zirconia surface treatments and the application of a composite interlayer between the zirconia substrate and the veneering on

the shear bond strength of zirconia-porcelain specimens. The PZI specimens (application of a composite interlayer between the porcelain and zirconia substrate with surface holes) ( $138\pm19$  MPa) showed a significant improvement of bond strength relative to the other groups {RZ (conventional zirconia-porcelain specimens), RZI (application of a composite interlayer between the porcelain the rough zirconia substrate) and PZ(porcelain bonded to zirconia substrate with surface holes)} ( $p<0.05$ ). Whereas, to the shear bond strength of PZ ( $100\pm15$  MPa) and RZI ( $96\pm11$  MPa) specimens were higher than RZ specimens ( $89\pm15$  MPa) the results are not significantly ( $p>0.05$ ). The application of porosity coupled with the composite interlayer produced a significant bond strength improvement (by ~55%) relative to conventional zirconia-porcelain specimens (RZ). The presence of the composite interlayer, despite its better mechanical properties relative to glass-ceramic (Table 8.2), did not contribute to significant increase in bond strength as reported in other studies on metal-ceramic adhesion (Aboushelib et al, 2006; Henriques et al, 2012; Henriques et al, 2011). Henriques et al. reported a bond strength increase of ~140% when a metal/ceramic composite interlayer was used between a metallic substrate and the veneering porcelain (Aboushelib et al, 2006). The optimization design of the zirconia-porcelain interface can be produced from the effect of high mechanical retention, promoted by the surface holes with the high strength and toughness. The zirconia particles distributed in the porcelain matrix acted as crack stoppers making more energy necessary for crack propagation, resulting in a significant improvement of mechanical properties (tensile strength, fracture toughness and hardness) relative to glass-ceramic. The heat pressing technique of porcelain to metallic and zirconia substrates have been shown to positively impact the porcelain cohesive properties and its adhesion to the substrate (Henriques et al, 2012; Aboushelib et al, 2008). The shear bond strength test results are characterized for not being influenced by the Young's Modulus of the alloy as happens for bending tests (Hammad and Talic, 1996) by its relatively uniform distribution of interface stresses (Hammad and Stein, 1991) by its suitability for evaluation of metal-ceramic and ceramic-ceramic bonds (Hammad and Talic, 1996; Anusavice et al, 1980). The device configuration is a important factor to guarantee the correct measures of the data. Therefore, this study showed that it is possible to highly enhance the zirconia-porcelain bond strength - even by~55% - by combining surface holes in zirconia substructures with the appropriate ceramic composite interlayer.

## ***Summarizing***

Summarizing the results of this thesis, this study supports the assumption that the zirconia powders in proportion (30% vol.%) and the use of interlayer has a strong influence on the mechanical properties of the porcelain-zirconia composites. The mechanical tests showed high performance these composites emphasizing the importance of the reinforcement in all-ceramic restorations. Improvements should be achieved by increasing of zirconia content up to 30% vol.%. Alternative zirconia-porcelain composites may allow to formation of a strong and aesthetics substructures. The hot pressing technique is an adequate technique to fabricate zirconia-porcelain composites to all-ceramic restorations. The fabrication of the restorations must be adapted and application guidelines must be adhered in order to ensure the quality of zirconia substructures (adhesion/interaction) and utilize the high potential of all ceramic materials. Besides, these materials revealed the importance of the deepening in studies related as the all-ceramic substructures and consequently increasing the mechanical characteristics and minimize the fracture risks on replacement of the natural teeth.

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## Main Conclusions and future perspectives

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The main conclusions and future perspectives of this thesis can be drawn:

### ***Zirconia commercial and synthesized***

- The CPM is a good technique to produce monophasic zirconia with different yttria content;
- Calcination temperature affected the characteristics of the synthesized materials;
- The zirconia commercial present the best characteristics to produce dental restorations compared as zirconia synthesized by CPM.

### ***Zirconia agglomerates and zirconia particles***

- The Yttria zirconia stabilized particles (ZP) presents the highest mechanical results when compared as Yttria zirconia stabilized agglomerates (ZA) incorporating in glass-ceramic matrix for all-ceramic substructures.

### ***Zirconia content in porcelain matrix***

- The zirconia particles up to 30% vol.% improve the mechanical properties (strength, toughness and hardness) of the porcelain-zirconia composites and lower values of the mechanical properties to composites with 40 and 50% vol.% and glass-ceramic (0% vol.%).

### ***Zirconia type in wear behavior***

- The type of zirconia powders influence directly in wear results and the pre-sintered particles (ZP) showed the best wear response compared as zirconia agglomerates (ZA).

### ***Zirconia content in wear behavior***

- The zirconia particles up to 30% vol.% presents the greater wear resistance than composites with 0, 10, 20, 40 and 50% vol.%.

### ***Ceramic-ceramic bond strength***

- The ceramic-ceramic bond strength was affected by surface treatment and presence of interlayer;
- The PZI specimens ((138±19 MPa) presents the best and significant results ( $p<0.05$ ) than RZ specimens (89±15 MPa);
- The PZ (100±15 MPa), RZI (96±11 MPa) and RZ (89±15 MPa) not present significant difference ( $p>0.05$ ).

## **Future perspectives**

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According the results presented in this study some future perspectives can be drawn:

- Influence of different contents of iron in colorimetric characteristics of yttria stabilized zirconia by CPM for dental applications.
- Influence of the zirconia particle size on the mechanical performance;
- Influence of the zirconia particle size on the wear behavior;
- Influence of the temperature and time of hot pressing technique on the mechanical properties of zirconia-porcelain composites;
- Influence of the yttria stabilized zirconia (3Y-TZP) content in porcelain on the dynamic mechanical analysis (DMA);
- Influence of yttria stabilized zirconia substructure surface treated on the shear bond strength;