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Towards the synthesis of an experimental bioactive dental ceramic. Part I: Crystallinity characterization and bioactive behavior evaluation

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HIGHLIGHTS

- Synthesis of a bioactive sol–gel dental ceramic for fixed prosthetic restorations.
- The sol–gel technique promoted the crystallization of leucite and a Ca–P phase.
- Sintering of DC80 induced no further crystallization of the material.
- An HCAp layer was developed on the specimens after 21 days of immersion in SBF.

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ABSTRACT

An attachment between the dental ceramic and the surrounding marginal tissues in fixed prosthetic restorations could eliminate secondary carries prevalence. The development of dental ceramics with apatite forming ability could provide the biological surface required for selective spread and attachment of specific cell types able to promote tissue attachment. Dental ceramics/bioactive glass composites synthesized by the sol gel method have been previously reported to develop carbonated hydroxyapatite (HCAp) in biomimetic solutions, requiring though a high amount of bioactive glass, which resulted in the compromise of their mechanical integrity. Thus, the aim of the present work was the synthesis and characterization of an experimental sol–gel derived dental ceramic with low amount of bioactive glass and the evaluation of its *in vitro* bioactivity.

Differential thermal and thermogravimetric analysis (TG–DTA), Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffractometry (XRD), Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) were used to evaluate the crystal structure and the *in vitro* apatite forming ability of the synthesized material. The results of this study indicated the successful sol–gel synthesis of an experimental dental ceramic containing low amount of bioactive glass that presented similar structural and morphological characteristics with a commercial feldspathic dental ceramic, while exhibiting *in vitro* bioactivity. The apatite forming ability of the experimental sol–gel derived feldspathic dental ceramic may trigger the appropriate cellular mechanisms towards the establishment of attachment with the surrounding connective tissue. This attachment could provide a barrier to oral bacteria penetration, prolonging the life expectation of the restorations.

1. Introduction

The metal–ceramic restoration consists of a metal substructure supporting a ceramic that is mechanically and chemically bonded to it [1]. The most widely used dental ceramics are feldspathic porcelains, which are composed of a glassy aluminosilicate matrix and at least one crystalline phase, leucite [2], the structure of which relies on a framework of $(Si,Al)O_4$ tetrahedra that form four-, six-

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and eight-member rings forming a sequence of parallel layers, passed through by open channels in the perpendicular direction, where potassium cations are placed [2,3]. Leucite acts as reinforcement agent and raises the overall thermal expansion of the bulk porcelain, due to its high coefficient of thermal expansion (CTE) leading to thermal compatibility with metal frameworks [4]. At room temperature leucite crystals are of tetragonal symmetry. When heated the $(Al,Si)O_4$ structure expands slowly by untilting and untwisting the rings until the symmetry changes to cubic at 625 °C [5,6]. Furthermore, the phase transformation of leucite from cubic to tetragonal when cooled, in combination with the greater contraction of the leucite crystals compared to the glassy matrix due to their large thermal contraction mismatch, cause tangential compressive stresses around leucite crystals. These stresses may act either as crack deflectors or crack initiators influencing the mechanical performance of the ceramic [2,7].

One of the most frequently described causes of failure of fixed metal–ceramic restorations, which shows an upward trend over the lifetime of the restoration, is secondary caries [8,9]. It is associated to plaque accumulation around marginal discrepancies and open marginal configurations of fixed dental prostheses that encourage microleakage of bacteria and their by-products during dissolution of the luting cement [10,11]. If hypothetically, connective tissue attachment, able to support a healthy junctional epithelium, could be established on the margins of fixed dental prostheses, would eliminate marginal discrepancies, cement dissolution and consequently secondary carries prevalence. Thus, the development of a cementum-like behavior of dental ceramics could provide the biological surface required for selective spread and attachment of specific cell types able to promote tissue attachment. As cementum consists of biological hydroxyapatite, it has been proposed that surface apatite formation on dental ceramics could comprise a step forward towards enhanced tissue attachment [12].

The bonding of bioactive glasses to hard tissues has been ascribed to a series of surface reactions that occur when the glass is exposed to an aqueous environment. Hench and Paschall [13], have described a sequence of five reactions that result in the formation of a carbonated hydroxyapatite (HCAp) layer on the surface of these bioactive glasses. The first reactions are the ion exchange between the alkali in glass and water. This is followed by a breakdown of the silica network, forming silanol bonds that re-polymerize to form a hydrated, high surface-area, silica-rich layer. This silica rich surface enhances the migration of Ca^{2+} and PO_4^{3-} groups to the surface forming an amorphous CaP layer, which is further crystallized in an HCAp layer. These reactions are summarized in the following five stages [14]:

Stage I: Rapid exchange of cations such as Ca^{2+} from the biomaterial with H^+ and H_3O^+ from the solution.
Stage II: Loss of soluble silica in the form of $Si(OH)_4$ to the solution resulting from breakage of Si–O–Si bonds and formation of Si–OH (silanols) at the glass solution interface.
Stage III: Condensation and re-polymerization of a SiO_2-rich layer on the surface depleted in alkali and alkaline earth cations.
Stage IV: Migration of Ca^{2+} and PO_4^{3-} groups to the surface forming CaO–PO_4 clusters on the top of the SiO-rich layer, followed by growth of the amorphous CaP.
Stage V: Crystallization of the amorphous CaP by incorporation of OH^-, CO_3^{2-}anions from the solution to form an HCAp layer.

Over the past years, several efforts have been made on precipitating apatite on conventional dental ceramics through modification with a bioactive glass. Specifically, Papadopoulou et al. [15], evidenced the growth of a well-attached carbonate apatite layer on the surface of a bioactive glass coated on a dental ceramic substrate after immersion in SBF solution. Furthermore, Kontonasaki et al. [16], reported that dental ceramic–bioactive glass composite mixtures supported the attachment and proliferation of human periodontal ligament cells. Sol–gel method has been reported to produce glasses and glass–ceramics with enhanced bioactivity, as it provides composite materials with fine porous textures and enhanced bioactivity compared to the melt-derived materials of the same composition [17]. In that direction, Chatzistavrou et al. [18], fabricated two novel sol–gel derived materials for dental applications; a glass–ceramic and a bioactive composite material (glass–ceramic 30 wt.%–bioactive glass 58S 70 wt.%) with characteristics similar to that of a commercial dental ceramic. The bioactive composite dental ceramic exhibited good control of composition, microstructure and properties, due to the intrinsic high homogeneity provided by the sol–gel method. Furthermore, sol–gel derived bioactive glass/dental ceramic composites with various ratios of a leucite-based fluorapatite glass ceramic have been previously synthesized [19] resulting in composite systems with enhanced bioactivity but low mechanical integrity. The addition of more than 50 wt.% fluorapatite dental ceramic resulted in non bioactive systems, probably due to the presence of fluorapatite crystals in the composition. Nevertheless, it is well established that glass–ceramics containing an apatite-like phase are several times less reactive than materials containing phosphorus in solid solution, while fluorinated hydroxyapatite is known to be less soluble by body fluids as compared to pure hydroxyapatite ceramics [20].

Consequently, the aim of this study was the synthesis, the qualitative identification of the crystalline content and the evaluation of the apatite forming ability of an experimental sol–gel dental ceramic, which has derived from the combination of a feldspathic dental ceramic and a well known sol–gel bioactive glass in low percentage. The hypothesis was that the newly synthesized dental ceramic would present similar structural and morphological characteristics with a commercial feldspathic dental ceramic, while it would present apatite forming ability.

2. Materials and methods

The experimental procedures included the fabrication and characterization of the experimental dental ceramic powder (DC80) in comparison with the starting materials, as well as the identification and qualitative determination of their crystalline content after being heat treated in order ceramic specimens to be fabricated. Additionally, the apatite forming ability of the fabricated specimens was evaluated. In details:

2.1. Fabrication of the experimental ceramic powder and construction of the sintered specimens

The bioactive glass (BG), the % weight ratio SiO_2:CaO:P_2O_5 was 60:36:4, as well as the novel dental ceramic composite (DC80) were prepared by the sol–gel method. In details, 13.2 mL tetraethyoxysilane (TEOS), 1.6 mL nitric acid, that was added to accelerate the hydrolysis reaction of TEOS, 0.7 mL triethyl phosphate (TEP) and 5.8 g calcium nitrate tetrahydrate ($Ca(NO_3)_2{\cdot}4H_2O$) were mixed with this order in 9.5 mL distilled H_2O. After mixing all the reactants, the sol was placed inside a furnace, where it was heated at 60 °C, while it was continuously stirred until gelation occurred. Finally, drying, ageing and chemical stabilization of the gel was performed by heat treatment stepwisely up to 700 °C [14]. In the case of the DC80, 80 wt.% of a leucite based dental ceramic (DC, IPS InLine®, Ivoclar, Schaan, Liechtenstein) was also added in the mixture, which was continuously stirred until gelation, in order the