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Rapid Communication

Development of an experimental glass ionomer cement containing niobium and fluoride

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Abstract

Glass ionomer cements (GICs) are currently used for various dental applications such as luting cements or as restorative materials. The calcium fluoro-alumino-silicate system is the basis for degradable glasses used to obtain the GICs. The purpose of the present paper is to add niobium to conventional glass system because according to previous papers niobium addition improves the chemical resistance and the mechanical properties of glasses. Therefore, the GICs prepared from these glasses would result in cements with higher chemical and mechanical resistance. The niobium fluoride powders were prepared using the sol–gel process and were characterized by X-ray diffraction, differential thermal analysis (DTA) and ^{27}Al and ^{29}Si MAS NMR. The results obtained by XRD showed that the powders prepared by this method are glass–ceramic. In the DTA curve was detected the presence of T_g and T_c temperatures. The analysis of MAS NMR spectra indicated that the framework of the powders is formed by SiO_4 and AlO_4 linked tetrahedra which are essential structures to yield the cements. Thus, we concluded that niobium fluoride silicate powders can be used in the preparation of GICs.

1. Introduction

The glasses based on the systems SiO_2–Al_2O_3–CaO or SiO_2–Al_2O_3–CaO–CaF_2 are used for the formation of polyalkenoate cements or glass ionomer cements (GICs) for dental applications [1–3] as a material for the restoration of anterior and posterior teeth, a cementing agent for the attachment of stainless steel crowns and bridges and as liners and bases. The properties which contributed to the great acceptance of GICs are adhesion to mineralized tissues, good biocompatibility, ability to bond chemically to tooth and release fluoride ions to confer resistance against secondary caries [4,5]. These properties could make the GICs ideal substitutes for the amalgam as a posterior filling material, as well as bone substitutes in maxillo-facial surgery.

Wilson and Kent developed the GICs in 1971 and according to them the most important compositional factor is the aluminium/silicon molar ratio, which became the glass network vulnerable to acid attack. In general these glasses require an Al/Si ratio between 1:2 and 3:5 to yield the GICs [6]. Thus, the compositions of these glasses are designed to be degraded by poly(alkenoic acids) in order to form the cements. Aqueous solution of poly(alkenoic acids) derived from organic acids such as poly(acrylic acid) is used to react with a finely powdered glass. The poly(acrylic acid) destroys part of the glass network releasing metal cations, such as Al^{3+} and Ca^{2+} that serve to form salt bridges between the polyacid chains causing the cement to set by gelation [4].

Conventional fluoride glasses from quaternary system SiO_2–Al_2O_3–CaO–CaF_2 are used in commercial GICs and they are prepared by fusion method. In the production batches, which involve heating the components at temperatures ranging from 1200 to 1550 °C, depending on the composition, fluorine is lost from the melt. This fluorine loss is uncontrolled and results in variable composition between batches [6]. Another problem with fluorine loss is the reaction with atmospheric moisture and the

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formation of hydrofluoric acid that attacks the crucible and the furnace.

Nowadays, soft chemistry has been used for the synthesis of glass because this route yields more homogeneous materials using lower processing temperatures than the conventional fusion method. The sol–gel method is based on the formation of an inorganic network by hydrolysis and polymerization of alkoxides in an aqueous medium and subsequent gelation [7]. This chemical process has the potential to yield glasses, which cannot be otherwise prepared by the conventional melting method due to their high melting points.

The development of new glass systems and methods for preparation of glasses is very important in dentistry to improve the properties of GICs. The properties of GICs are dependent on the specific chemical and physical formulation of glasses and considerable efforts have been made to improve the properties of GICs using other types of glass powders derived from calcium fluoro-aluminosilicate systems with new components. Therefore, it is very important to carry out research about the presence of fluoride or other ion contents of the glasses.

In our previous work, niobium silicate glasses were developed for use as GICs. The properties of cements prepared from these glasses were similar to the ones from commercially available cements, indicating that niobium can improve the mechanical characteristics of these materials [8]. Unlike the glasses reported in this study, commercial ionomer glasses contain fluoride because it improves the working characteristics of the cement paste and contributes to inhibit the secondary caries. In order to satisfy this commercial requisite, in this work fluoride was added to the niobium silicate glass composition using a chemical process.

2. Experimental procedure

2.1. Preparation of powder samples

The powder samples in the $4.5SiO_2–3Al_2O_3–xNb_2O_5–2CaO–3CaF_2$ system were prepared using the sol–gel process, with composition $0.10 < x < 1.0$.

The reagents used to prepare the powders were tetraethoxysilane (TEOS, 99%, Aldrich), aluminum nitrate nonahydrated (99%, Aldrich) calcium nitrate (99%, Synth) niobium citrate solution and H_2SiF_6 (fluorsilicic acid solution 25%, Aldrich).

In the sol–gel route, TEOS was first hydrolyzed in ethanol using an open vessel under continuous stirring at room temperature for 1 h. The previously dissolved aluminum and calcium salts were then added drop wise to the hydrolyzed TEOS solution and afterwards niobium citrate solution and H_2SiF_6 were added to the solution. The fully mixed solution was then heated with continuous stirring until 80 °C, when gelation occurred. In order to obtain the powder samples, the gel was dried at 80 °C, pulverized and then slowly fired for 1 h at each of the following temperatures: 250 °C, 400 °C, 600 °C and 700 °C using an electrical oven.

2.2. Powder samples characterization

The prepared powders were analyzed by X-ray diffraction (XRD) using Cu Kα radiation, 42 KV, 0.020°/min and a scan range of 20–70°. The diffractograms were obtained in an automatic diffractometer (Rigaku model Rint 2000). The differential thermal analysis (DTA) was carried out in the equipment (TA Instruments) using the following experimental conditions: α-alumina (reference), sample weight = 20 mg, heating rate = 10 °C/min and a N_2 atmosphere. Magic-angle spinning nuclear magnetic resonance (MAS–NMR) ^{29}Si and ^{27}Al were used to investigate the structural aspects of the powders. MAS–NMR spectra were acquired using a spectrometer (Varian Unity Inova 300). ^{29}Si–NMR (59.5 MHz) spectra were obtained with a zirconium rotor using π/2 pulses of 4.5 μs and were referenced to tetramethylsilane (TMS). ^{27}Al–NMR (78.15 MHz) spectra were obtained with π/6 pulses of 2 μs in a Si_3N_4 rotor and were referenced to $Al(H_2O)_6^{3+}$.

3. Results

Fig. 1 indicates the XRD profile of powders with fluoride and niobium fired from 400 to 850 °C. As can be seen all the powders containing Nb and fluoride are glass–ceramics and presented crystalline phase of fluorite (CaF_2) and calcium aluminium silicate ($Ca_3Al_6Si_2O_{16}$) and calcium fluorosilicate ($Ca_4Si_2O_7F_2$). Conversely, all the non-fluoride powders prepared are completely amorphous [8].

The DTA curve for powder containing Nb and fluoride is shown in Fig. 2. The DTA curve shows the presence of a glass transition temperature (T_g) and the temperature of crystallization (T_c). The T_g and T_c values for the niobium silicate glass prepared by chemical processing are shown in Table 1.

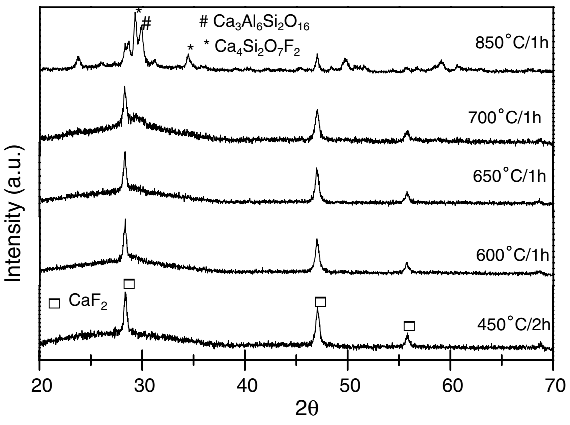

Fig. 1. XRD patterns of powders thermally treated: 400 °C; 600 °C, 700 °C and 850 °C.