Bioceramics 22 (2009) pp399-403
www.bioceramics22.com

Sol-gel fabrication of glass-ceramic composite materials for dental application

X. Chatzistavrou[1], D. Esteve[1], E. Hatzistavrou[2], E. Kontonasaki[3], K.M. Paraskevopoulos[2] and A.R. Boccaccini[1]

[1]Department of Materials, Imperial College London, Exhibition Road, London SW7 2AZ, UK
[2]Physics Department, [3] School of Dentistry
Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece
kpar@auth.gr,

Keywords: Composite materials, sol-gel technique, bioactivity, coating, FTIR, SEM, DTA

Abstract.

The aim of this study was to investigate the sol-gel technique to fabricate glass-ceramic composite materials. The produced materials have potential application in dental restorations and they are expected to exhibit better control of composition, microstructure and properties due to the intrinsic processing benefits of the sol-gel preparation method. The characterization of the fabricated composites was performed by a range of techniques. The microstructure and bioactive behavior of the materials before and after application of heat treatment were studied. Moreover, the capability of making coatings on dental glass-ceramic substrates using the new glass-ceramics was demonstrated. The formation of well attached coatings exhibiting bioactive behavior was presented.

Introduction

Dental ceramics used in restorative dentistry exhibit a combination of properties such as durability in the oral environment, resemblance with natural tooth structure, high strength, fracture toughness and wear resistance [1]. These stringent requirements have led to further research in the field of dental ceramics in order to further develop improved materials with improved properties and bioactive function. The sol-gel process involves synthesis of materials by exploiting the transition of a system from the liquid phase to a porous solid allowing the fabrication of new inorganic materials with controlled mictrostructure and properties. One of the significant advantages of the sol-gel method is the ability to synthesize silicate glasses at low sintering temperature enabling the preparation of glass-ceramics with special compositions which are not possible to be obtained by melting [2].

This work investigates the application of the sol-gel technique for the fabrication of glass-crystalline composite materials with potential use in dental restoration. These composite materials aim to create a bioactive surface around the margins of fixed restorations which could lead to periodontal tissue attachment, providing complete sealing of the marginal gap between tooth and fixed prosthesis.

Materials and Methods

Two composite materials were fabricated. The first composite (COMP1) was fabricated by modifying the sol-gel bioactive glass 58S through the incorporation of a commercial porcelain (IPS Classic Margin, Ivoclar, Schaan, Liechtenstein). Bioactive glass 58S was prepared by the sol-gel method as described in detail in the literature [3]. The other composite material (COMP2) was fabricated by mixing and stirring the precursor solution of the bioactive glass 58S with the respective precursor solution of a new sol-gel glass-ceramic in the system SiO_2 60 - P_2O_5 3 - Al_2O_3 14 - CaO 6 - Na_2O 7- K_2O 10 (wt %). The new glass-ceramic was synthesized by sol-gel process using DI water and nitric acid, tetraethoxysilane (TEOS), triethylphosphate (TEP), aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$),

potassium nitrate (KNO_3), sodium nitrate ($NaNO_3$) and calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$) as precursors. In all cases the final solution was converted to a gel by a drying process at temperatures of up to 180°C, while the stabilization was performed by heat treatment up to 700°C. The fabricated materials were characterized by Fourier Transform Infrared Spectroscopy (FTIR) (PerkinElmer Multiscope), in the range 5000-400cm^{-1}, Scanning Electron Microscopy (SEM) (JEOL JSM-840A). Differential Thermal Analysis (DTA) Stanton Redcroft STA 780) was also performed up to Tmax=1100°C with heating rate 20°C/min. The characteristics of these materials were compared to those of a commercial dental ceramic. Moreover the bioactive behaviour was investigated through immersion in Simulated Body Fluid (SBF) for 3, 7, 10, 15 and 20 days [4]. The immersed samples were in form of pellets fabricated by cold-pressing (m=100mg) and heat treated up to 950°C with heating rate 80°C/min for COMP1 and up to 980°C with heating rate 30°C/min for COMP2. Moreover, the ability of the novel composites to be applied as coatings on substrates of dental porcelain was investigated. In each case a thick slurry was prepared by mixing each powder of the composite materials with a modelling liquid (IPS Classic Margin Build-Up Liquid). The slurry was spread by a spatula on substrates of dental porcelain. The fabricated specimens were exposed to specific heat treatment for each case. The quality of the attachment was investigated by optical microscope and SEM on cross sections of the specimens. Microhardness measurements were performed on the coatings (Microhardness tester Indentec Zwick/Roell ZHV, Zwick GmbH, Ulm, Germany) using a Vickers diamond indenter and loads of 5 N (500 g) for 10 s. The bioactivity of the fabricated coatings was also determined.

Results and Discussion

The SEM images of the fabricated composites (figure 1) show the porous morphology of both composites.

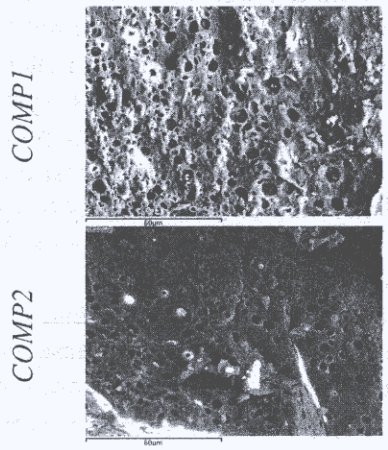


Fig. 1: SEM images of the porous structure of the fabricated composite materials.

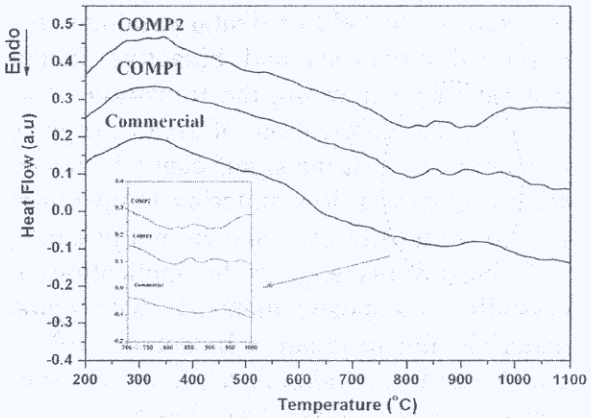


Fig. 2: DTA curves of composite materials. The respective curve of the commercial glass-ceramic is presented for comparison.

The thermal analysis of the fabricated materials shows evidence of the crystallization process corresponding to the characteristic crystalline phases expected (Fig.2). Exothermic peaks were observed in both DTA curves in the temperature range 800-1000°C, which is the temperature range where crystallization of wollastonite phase occurs (~900°C). The DTA curve of the commercial glass-ceramic does not present any characteristic feature in the same temperature range.

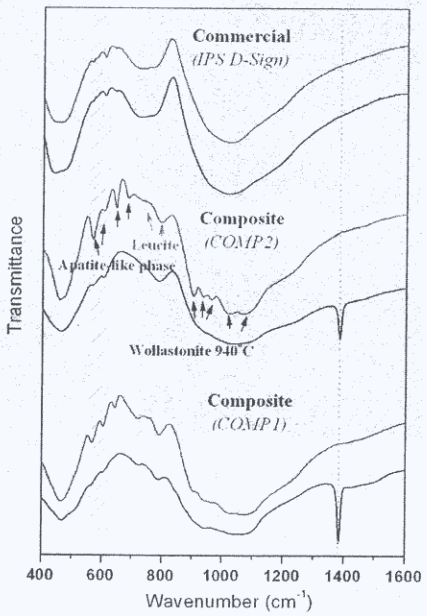


Fig. 3: FTIR spectra of the new glass-ceramic material (black line) and the commercial glass-ceramic (blue line).

The transmittance spectra of COMP1, COMP2 and the commercial material are presented in Fig. 3, before (black lines) and after (red lines) the application of a heat treatment up to 1000°C with 20°C/min. The specific heat treatment was selected for the identification of the phases which are formed regarding the results occurred by the DTA analysis. The spectra of the composites after heat treatment show the raise of some new peaks. These new peaks around ~645cm^{-1}, ~685cm^{-1} and in the range 900-1080cm^{-1} are assigned to the formation of wollastonite phase, while the replacement of the broad peak at 700-800cm^{-1} by the shoulder at 720cm^{-1} and the sharper peak at 780cm^{-1} in the spectra confirm the growth of the leucite crystalline phase [5]. The increase of crystallinity of the apatite phase after the applied heat treatment is also observed. Additionally, heat treatment causes the disappearance of the peak at 1384cm^{-1}, which confirms the release of the NO_3^- groups from the network of the fabricated composites. Moreover, the spectra of the commercial glass-ceramic present all the characteristic peaks of an aluminosilicate network without having any change in the structure after the applied heat treatment.

SEM images of the surface of the pellets of the composite materials before and after immersion in SBF are shown in Fig. 4. The composite samples exhibited the growth of a thick, uniform and crystalline carbonated hydroxyapatite layer (HCAp) on the surface of the pellets even after 3 days of immersion in SBF, while further immersion in SBF for up to 20 days confirmed that the developed layer is retained on the surface of the samples.

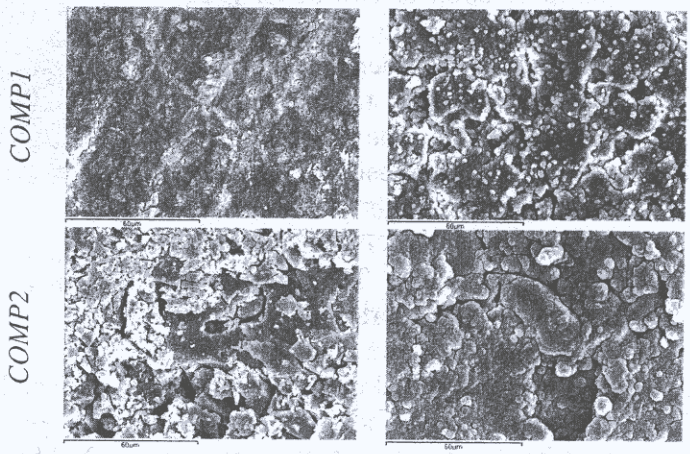
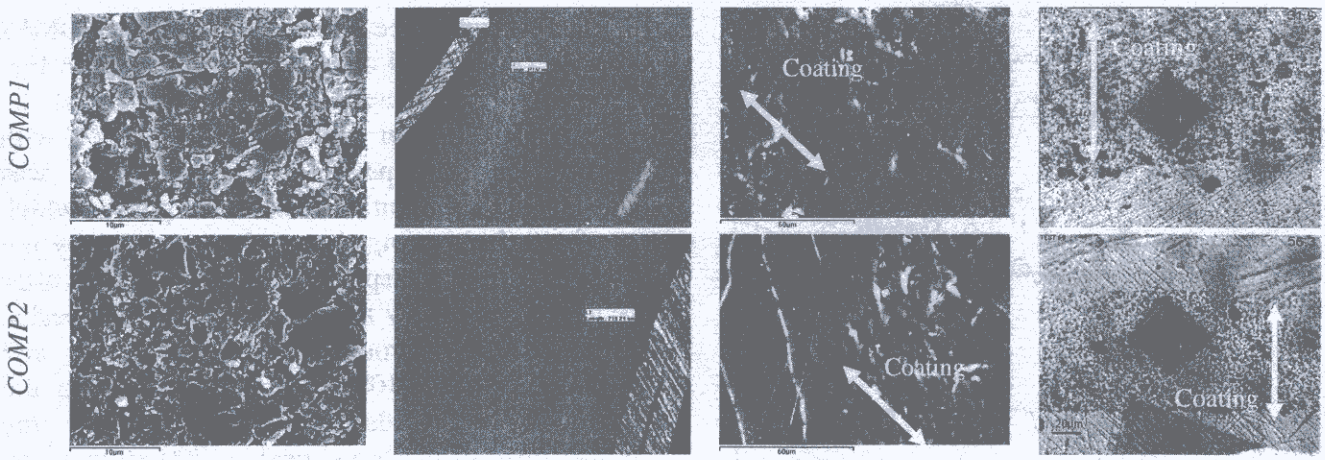


Fig. 4: SEM images of the formed HAp layer on the surface of both COMP1 and COMP2 pellets after 3 days in SBF.

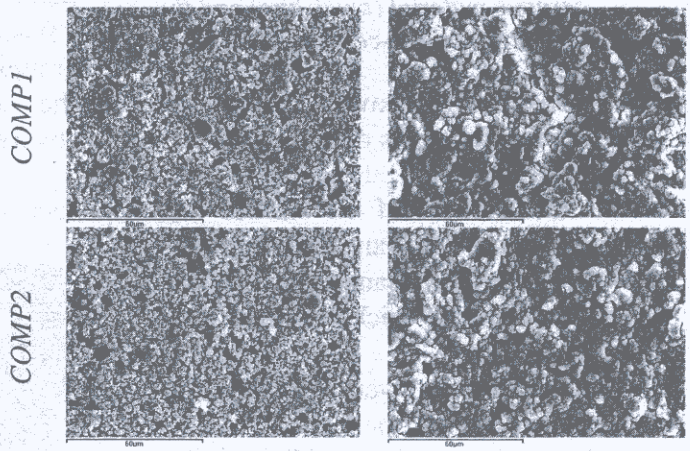
In order to assess the feasibility of using the developed materials as coating in dental applications, the bioactive composite material was applied on substrates of dental materials and the coating attachment to the substrate as well as the hardness of the fabricated coatings were investigated. Images were taken by optical microscopy from cross sections of the coated specimens (Fig. 5). The very good attachment of the coatings on the substrates was confirmed qualitatively. Microhardness testing indentations gave an average value of ~30HV for COMP1 and ~60HV for COMP2. The higher value for COMP2 is related to the applied heat treatment. The microhardness of COMP2 is similar to values of sol-gel derived materials.



SEM images. Surface morphology | *Optical microscopy image. Cross section* | *SEM images. Interface attachment* | *Optical microscopy image. Microporous structure*

Fig. 5: Coated specimens.

Coated specimens after their immersion in SBF presented bioactive behavior similar to the one which was observed in case of the respective pellets. The growth of HAp layer on their surface occurred after 7 days of immersion in SBF (Fig. 6).



Before SBF *After 3d in SBF*

Fig. 6: SEM images of the formed HAp layer on the surface of both COMP1 and COMP2 coated specimens after 7 days in SBF.

Conclusions

The fabrication of two novel glass-ceramic composite materials with potential use in dental restoration by the sol-gel technique was demonstrated. The new glass-ceramic composites present characteristics slightly different to those of a commercial leucite based dental ceramic. The bioactive behavior of the fabricated materials was assessed. The feasibility of using the developed materials as coating in dental applications was confirmed. The very good attachment of the coatings to the substrate in both cases was observed, while the higher microhardness value of the specimens coated by COMP2 is attributed to the specific applied heat treatment.

Acknowledgements

One of the authors (X.C) acknowledges the funding of European Commission via a Marie Curie Fellowship.

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