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Preparation and characterisation of porous composite biomaterials based on silicon nitride and bioglass

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Abstract

The combination of bioinert and bioactive material offers new potentialities in bone tissue engineering. The present paper deals with preparation of novel biomaterial composite based on silicon nitride (Si_3N_4) and bioglass (in amount of 10 and 30 wt%) by free sintering at 980 °C for 1 h in nitrogen atmosphere. The obtained material was characterised by differential thermal analysis (DTA) and X-ray powder diffraction (XRD), porosity and pore size distribution were evaluated by means of mercury intrusion porosimetry (MIP). The bioactivity was examined in vitro with respect to the ability of hydroxyapatite layer formation on the surface of materials as a result of contact with simulated body fluid (SBF). All composites were studied by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) before and after immersion in SBF. The bioglass-free sample was prepared as a reference material to compare the microstructure and bioactivity to the composites.

Keywords: A. Sintering; B. Composites; D. Glass; D. Nitrides; E. Biomedical applications

1. Introduction

Silicon nitride (Si_3N_4) based ceramics represent a combination of mechanical, tribological, thermal and chemical properties that makes them suitable for high performance components in severe environments in several industrial applications, such as cutting tools, ball bearings, sealing elements and engine components. These properties, namely hardness, fracture toughness, friction and wear coefficient, are also very important for many high-load medical applications of bioceramics in the human body. Another desirable property of ceramic-based implants is bioactivity.

On the basis of potentialities, silicon nitride attracts interest for orthopaedic and dental applications [1–10] in the human body, but is not yet established as a biomaterial in medicine. This is related to some controversy in the literature about the biocompatibility [1,4–6]. Several works on biocompatibility and bioactivity of silicon nitride outline that silicon nitride based ceramics can be used as materials for clinical applications in the field of hard tissue surgery. The absence of toxic behaviour was ascertained during toxicity tests [11].

In the application of silicon nitride as a biomaterial a key aspect is the presence of grain boundary phases deriving from the necessary use of sintering aids. The grain boundary phase composition and amount depend on the selected additives which, during sintering, react with the silica presents on the silicon nitride particles and other impurities, leading to the formation of a liquid phase. This allows the sintering of silicon nitride, but the final dense ceramics contains amorphous or partially crystalline grain boundary phases. It has to be taken into account that the glassy phases may exhibit bioactivity different from silicon nitride crystalline phases. Generally used additives for sintering of silicon nitride there are Mg, Al, rare earth and bioactive glass as novel sintering aid [12].

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The first bioactive material reported was a four component glass composed of SiO_2, CaO, Na_2O, and P_2O_5 by Hench et al. in 1971 [13]. Bioglass® 45S5 has the following chemical composition: 45.0 SiO_2–24.5 Na_2O–24.5 CaO–6.0 P_2O_5 in wt%. It is a silicate glass based on the 3-D glass forming SiO_2 network in which Si is fourfold coordinated to O. The key compositional features that are responsible for bioactivity of 45S5 glass are its low SiO_2 content (compared to more chemically durable silicate glasses), high Na_2O and CaO (glass network modifiers) content, and high CaO/P_2O_5 ratio [14]. When implanted, the low silica content and the presence of sodium ions in the glass results in very rapid ion exchange with the protons and hydronium ions of physiological solutions [15]. The ion exchange creates an alkali pH at the implant interface with the body fluids, leading to nucleation and crystallisation of hydroxyl carbonate apatite (HCA) bone mineral at the surface of the glass. The growing bone mineral layer bonds to collagen, produced by the bone cells, and forms a strong interfacial bond between the implant and the living tissue [16,17].

However, medical applications of bioglass have been centred on low stress fields, mainly due to its non-adequate fracture toughness compared to that of cortical bone. This limitation is unfortunately a common characteristic of glasses, ceramics and glass ceramics used in medical applications.

Theoretically, Si_3N_4–bioglass composites would lead to medical implants that combine the advantageous properties of each material individually. Amaral et al. and Santos et al. [3,18] have prepared almost fully dense Si_3N_4–bioglass composite by hot pressing technique with exceptional mechanical properties that make it suitable for high-load applications. Preliminary in vitro studies have demonstrated that under specific conditions Si_3N_4–bioglass composites have the ability to form an apatite layer on their surface. The bioactivity evaluation was carried out using a simulated body fluid (SBF) and the apatite formation was characterised by X-ray photoelectron spectroscopy (XPS) [18]. The present work describes the preparation of porous bioactive composite, based on silicon nitride and 45S5 Bioglass®, using free sintering. Our choice of the pressureless sintering stems from its attractiveness as a simple, reproducible and economic method that allows preparing material with different pore size. A complete description of preparation, sintering, mechanical and microstructural characterisation and also bioactivity is reported. Scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) were employed to investigate the morphological changes of the surface and the structure of the grown layer respectively.

2. Experimental procedure

2.1. Preparation and characterisation of the samples

Si_3N_4–bioglass composites were prepared from a mixture of a Si_3N_4 commercial powder (Yantai, Tomley Hi-Tech Ind. & Tra. Co., Ltd., $D_{90}=1.0$ μm, $O<1.4\%$) and a bioglass. The bioglass (with the similar composition to Bioglass® 45S5) was prepared by a sol–gel method according the procedure [19] and has the following chemical composition: 45.0 SiO_2–24.5 Na_2O–24.5 CaO–6.0 P_2O_5 in wt%. The bioglass powder was then mixed with Si_3N_4 powder in a 0–30% weight proportion in isopropanol by planetary milling for 2 h in a silicon nitride jar using silicon nitride balls. The homogenised suspension was dried and subsequently screened through 71 μm sieve in order to avoid large hard agglomerates. The pellets were uniaxially pressed at 100 MPa. The samples were free sintered at 980 °C for 1 h in nitrogen atmosphere. After the dwell time the samples were taken out from the furnace to inhibit the crystallisation of the bioglass as, according to Clupper and Hench [20–23], who carried out quantitative investigations on the effect of crystallinity on the apatite formation on Bioglass® surface in vitro, the crystal phase $Na_2Ca_2Si_3O_9$ slightly decreased the formation kinetics of an apatite layer on the Bioglass® sample surface but it did not totally suppress the formation of such a layer [20]. The sintering temperature of the composites was chosen on the basis of results obtained from the differential thermal analysis (DTA). The analysis was performed on TA Instruments Q600 equipment using a heating rate of 10 °C/min and Al_2O_3 as reference.

The bioglass-free sample (referred as Si_3N_4-0) was prepared as a reference material to compare the microstructure and bioactivity to the composites. The sample was sintered in air at 1150 °C for 1 h. The experiments have shown that the oxidation of pure Si_3N_4 is negligibly slow at temperatures under 1200 °C [24]. The composition of studied systems is listed in Table 1.

The densities of the samples were measured by the Archimedes method in water. The theoretical densities were calculated according to the rule of mixtures. The microstructure was observed by scanning electron microscopy (Zeiss, EVO 40 HV, Germany). The elemental analysis of crystalline phases was examined by EDX. The crystalline phases present in the ground samples were identified using X-ray diffraction (XRD) (Bruker AXS D8 Discover X-ray diffractometer). Identification of the structural groups of the composites before and after soaking in SBF solution was carried out by Fourier transform infrared (FTIR) spectroscopy. The FTIR spectra were obtained using a Nicolet 6700 FTIR spectrometer from Thermo Scientific, equipped with an IR source, KBr beam-splitter, and DTGS KBr detector. Samples were analysed using Smart Orbit™ horizontal single-reflection ATR accessory featured with diamond crystal. For each sample, 64 scans in the 4000–400 cm^{-1} spectral range were recorded with a resolution of 4 cm^{-1}. Vickers hardness (HV) and fracture toughness (KIC) were measured using Leco hardness tester (LV-100, Leco Co., USA). The pore size distribution was determined by mercury intrusion porosimetry (Pore Master 60).

Table 1
Chemical composition of studied systems.

Sample	Composition (wt%)	
	Si_3N_4	45S5 Bioglass®
Si_3N_4-0	100	0
Si_3N_4-10	90	10
Si_3N_4-30	70	30