



Catalysis, nanostructure and macroscopic property triangle in bioactive calcium-containing ceramic systems

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ABSTRACT

Calcium silicate ceramics are intended for application as long-term implant materials. In the present work, attention was paid to understand the correlations between the nanostructure (aggregate size, crystallinity, porosity) and the macroscopic properties (solubility in water and simulated body fluids, SBF; hardness) varying the chemical composition. Varying the catalyst (from a base to various acids) during the chemical synthesis was shown to significantly impact on the pore size, crystallinity and mechanical properties. The basic catalyst yields the ceramics with the highest mechanical strength. Ammonia used in 1.0 or 10.0 molar ratio results in bulk ceramics with parameters required for a biomedical application, good hardness (180–200 HV) and low solubility (1–3%) in water and in SBF. The fine porosity (~50 nm) and homogeneous amorphous structure induce good mechanical character.

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1. Introduction

The bioactive glass-ceramics and composites have been successfully used for the repair, reconstruction, and replacement of diseased or damaged parts of the body, especially bone or tooth. The most bioactive glasses and ceramics have been based on a silicate network due to the slight and slow solubility of silicates in human body fluid. Hereby these bioactive materials can be used as long-term implants. The bioactivity can be attributed to the bone bonding behavior. On the surface of bioactive materials, a biologically active carbonate hydroxyapatite (HCA) layer forms which provides the bonding interface with the living tissues. The growth rate of the HCA layer mainly depends on the bioactive glass composition and the porosity. The lower SiO₂ and higher CaO contents result in a higher apatite layer growth, while the larger surface area (> natural bone porosity) and smaller pore size reduce the growth rates of the apatite layer [1–7]. Studying the “in vitro behavior” of the glasses indicates that the presence of phosphorus in the glass composition is not an essential requirement for the development of the HCA layer [1–8]. The apatite layer forms in the P₂O₅-free calcium silicate glasses using the phosphorus content present in the in vitro solution.

The gel-derived ceramics have been demonstrated to have better bioactivity than melt-quenched ceramics [9–13]. The better bioactivity can be explained by the great differences in the textural properties (e.g. in the porosity) of the gel- and melt-derived materials [11–13] and the better homogeneity, purity and amorphous feature of the sol-

gel ceramics [11–16]. Furthermore, the amount and the position of crystalline particles can be much easier controlled via sol–gel than melting processes.

In our previous work, acid- or base-catalyzed sol–gel routes have been developed for the synthesis of calcium silicate systems [17,18]. The effect of the chemical composition, notably the catalysts on the bond systems has been investigated [19]. The present work focuses on the determination of the correlations between the ceramic nanostructure (particle size, crystallinity, and porosity) and the macroscopic properties (solubility in distilled water and simulated body fluids; hardness) achieved by using various catalysts (ammonia, acetic acid, and phosphoric acid). Dynamic light scattering (DLS) and scanning electron microscopy (SEM) provide the size characterization. The crystalline phases, morphology, and chemical composition of the particles with different shapes have been analyzed by X-ray diffraction (XRD), SEM, Fourier transform infrared spectroscopy (FTIR), and energy dispersive X-ray spectrometer (EDX).

2. Experimental

2.1. Materials and gel synthesis

The calcium silicate gel samples were produced by sol–gel technique starting from tetraethoxysilane (TEOS), (Si(OC₂H₅)₄, 98%, Aldrich) and calcium nitrate tetrahydrate, (Ca(NO₃)₂·4H₂O, 99%, Reanal) as precursors; 1-propanol (at. Aldrich) as solvent; ammonia (25% aqueous solution, Reanal), acetic acid (99–100%, Reanal) and phosphoric acid (85% aqueous solution, Reanal) as catalysts. The syntheses of materials were

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carried out by hydrolysis and polycondensation in an organic solution of stoichiometric amounts of the precursors. The rate of the catalyst concentrations (0.50–10.0 mol catalyst/Si) was varied during this synthesis series. The gelation time of starting organic solution was 1 h in basic (NH_3 solution) or in phosphoric acid catalyzed processes, and 24 h in acidic solution (acetic acid). The aging as well as the drying processes were performed at 80 °C [8–10]. The heat treatment i.e. the sintering of ceramic powders was conducted in two steps, first at 600 °C (30 min) and after pressing the pellets (uniaxial pressing at 24.5–39.2 MPa for 15–20 min/pellets) at 700 °C (3 h, 100 °C/min heating and 20 °C/min cooling rates).

2.2. Characterization methods

The aggregate size of ceramics powders has been determined by *dynamical light scattering* (DLS) method. DLS measurements were performed by means of an equipment (Brookhaven) consisting of a BI-200SM goniometer and a BI-9000AT digital correlator. An argon-ion laser (Omnichrome, model 543AP) operating at 488 nm wavelength and emitting vertically polarized light was used as the light source. The signal analyzer was used in real-time “multi tau” mode. In this mode the time axis was logarithmically spaced over an appropriate time interval and the correlator used 218 time channels. The pinhole was 100 μm . The particles were generally dispersed in ethanol for DLS measurements instead of distilled water in order to avoid the aggregation of the particles in distilled water. The number-weighted particle size distribution was detected by DLS.

The particle size and morphology of ceramic powders and sintered pellets have been studied by a FEI Quanta 3D FEG *scanning electron microscope* (SEM). The SEM images were prepared by the Everhart-Thornley secondary electron detector (ETD), its ultimate resolution is 1–2 nm, and the accelerating voltage is 15.0 kV. Since the conductance of the particles investigated is high enough to remove the electric charge accumulated on the surface, the SEM images were performed in high vacuum without any coverage on the specimen surface. For the best SEM visibility, the particles were deposited on a HOPG (graphite) substrate surface. SEM combined with energy disperse X-ray spectroscopy (EDX) is mainly applied for spatially resolved chemical analysis of bulk samples.

Wide-angle x-ray scattering (WAXS) were detected with a 1D MYTHEN detector in HASYLAB of DESY (Hamburg). The WAXS data were collected over the 2θ -range of 7–30° with a step size 0.0212°. Identification of phases was achieved by comparing the diffraction patterns with the standard PDF cards.

The mechanical properties of bulk ceramics were compared with *Vickers hardness* measurements. The compressed tablets were tested with various instruments (an Akashi Microhardness tester, Anton Paar Microhardness tester MHT 4, and Shimadzu DUH-202 tester). A pyramidal diamond indenter was applied to the tablet surface under a load of 0.5–2 N for 15 s. The tests were repeated at three different places 5–20 times for each sample.

The surface area and porosity of ceramic samples were characterized by CCl_4 sorption analysis at 25 °C on an autosorb computer controlled surface analyzer (AUTOSORB-1, Quantachrome or ASAP 2010 Micrometrics). Each sample was degassed for 12 h prior to analysis.

The *solubility* of the ceramics has been investigated in distilled water as well as in simulated body fluid (SBF) [20]. In all cases the sintered bulk samples were soaked for 1–14 days in distilled water and for 3 days in SBF. The drying process took for 2 h at 180 °C and 2 h at 700 °C after distilled water treatment and for 10 days at room temperature after dipping in SBF, respectively. Parallel tests have been carried out on ten samples. Weight changes, chemical surface modification, and the ions eluted into solution (in tissue culture water after 7 days) were fully analyzed.

The ions dissolved in distilled water were analyzed with *total reflection X-ray fluorescence* (TXRF) spectroscopy. The TXRF measurements

were performed with an Atomika 8030C (FEI Co.) instrument. The influence of SBF soaking on the surface was monitored by *attenuated total reflectance* (ATR) *Fourier transform infrared* (FTIR) spectroscopy. The FTIR measurements were performed on Bruker IFS 55 instrument with diamond ATR head (PIKE technology). The infrared spectra were collected over the range of 4000–550 cm^{-1} at a resolution of 0.5 cm^{-1} .

3. Result and discussion

The calcium silicate ceramic systems were synthesized by acid- or base-catalyzed sol-gel routes [17,18]. A Ca- and Si-containing colloid (gel or sol) systems form in the first step of the sol-gel method. The ceramic products can be obtained by drying and sintering processes from the gel system. The main reactions of the gelation are the hydrolysis and condensation. The hydrolysis and condensation reactions require acid or base catalysis [17,18].

The previous research has studied the effect of the chemical parameters (e.g. catalysis, Ca/Si and catalyst/Si ratios) and the heat treatment on the bond systems and aggregate structures. The acid-catalyzed reactions produce a gel system with randomly branched network arising from the fast hydrolysis. The base-catalyzed reactions yield a sol system built up from aggregates due to longer hydrolysis time, which can provide the possibility for the aggregation of particles into the most thermodynamically stable arrangement [19]. The NH_3 catalyst favors the formation of $=\text{Si}(\text{OSi})_2$ units ($\text{SiO})_2\text{Si}(\text{O}^-)_2$ or $(\text{SiO})_2\text{Si}(\text{OH})_2$. The Ca ions prefer the bond to $=\text{Si}(\text{OSi})_2$ units [19]. The Ca ions bond not only to the silicate matrix or silicate anions in a crystalline phase, but also to the carbonate as well as OH ions in the range of 160–500 °C. According to the XRD data, CaO does not form in these sol-gel derived ceramics up to 1000 °C.

3.1. Comparison of various types of catalyst

In Table 1, the porosity data and the particle sizes represent the structural parameters; while the Vickers hardness values (HV) the mechanical properties. For better comparison, the samples of presented investigations were synthesized with the same compositions (1:1:1 molar ratios of Si/Ca/catalyst) and sintered at 700 °C, only the type of catalysts was varied.

The ceramic products prepared by base catalysis possess the best *mechanical strength* (around 200 HV); this result is promising for a biomedical application. The sample of phosphoric acid catalysis shows altering HV values (on average 120 HV) due to the inhomogeneous phase composition (Fig. 1). The acetic acid catalysis produces low HV values (42–52 HV).

The big differences between the HV data may be explained by the *porosity* (Table 1) and the crystalline phases. The porosity of the ceramic systems is one of the important features with respect to the medical application. For comparison, the average specific surface areas of the cancellous and cortical human bone are 50–100 $\text{m}^2 \text{g}^{-1}$ [21,22] and 2–40 $\text{m}^2 \text{g}^{-1}$ [21,23,24], respectively. The total porosity

Table 1
Structural and mechanical data of ceramic samples synthesized with different catalysts.

Measurements	Ammonia	Acetic acid	Phosphoric acid
Vickers hardness (HV)	190 ± 20	47 ± 5	120 ± 50
Porosity (%) (SEM)	17 ± 3	8 ± 2	15 ± 2
Specific surface area ($\text{m}^2 \text{g}^{-1}$) (CCl_4 adsorption)	19 ± 3	7 ± 2	14 ± 1
Pore size (range/average in nm) (SEM)	20–240/50	20–2000/165	40–1500/310
Particle size (range/average in nm) (DLS)	50–180/90	80–120/100	150–600/300
Particle size (range/average in nm) (SEM)	45–120/75	30–110/90	90–180/119

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