Bioactive ceramic composites sintered from hydroxyapatite and silica at 1200°C: preparation, microstructures and in vitro bone-like layer growth

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Abstract Bioceramic composites were synthesized by sintering the powders of hydroxyapatite (HAp) mixed directly with additive of 0.5, 1.0, 2.0, 5.0 and 10 wt.%SiO2, respectively, at 1200°C. X-ray diffraction (XRD) analysis indicated that the phase transformation from HAp to tricalcium phosphate (TCP) comprising α-TCP and Si-TCP occurred and became more prominent with the addition of SiO2 and the increase in SiO2 content. The observations of their surface microstructures showed that the addition of SiO2 suppressed the grain growth and promoted the formation of crystalline-glassy composites denoted HAp + TCP/Bioglass. As the SiO2 content is as high as 5 wt.%, the composite made a feature of crystalline clusters with different sizes consisting of HAp and TCP grains surrounded by the matrix of glassy phase. Furthermore, the dependence of in vitro bioactivity of these composites on the SiO2 content was biomimetically assessed by determining the changes in surface morphology, i.e., bone-like apatite layer growth, after soaking in an acellular stimulated body fluid (SBF) for 3 days at 36.5°C. It was found that the HAp-SiO2 composites showed a much faster bone-like layer growth than pure HAp, and the propensity of composites to exhibit a better bioactivity was getting more notable with increasing SiO2 content, except for the case of the highest content of 10 wt.%.

1. Introduction

Different kinds of materials such as ceramics, polymers, transplanted cells and bioactive molecules have been used to regenerate bone in combination with some novel techniques [1]. As an ideal medical implant material, the synthetic calcium phosphate ceramic of hydroxyapatite (HAp) has been given the most common investigations since the major mineral constituent of such an osteoconductive and biocompatible material is quite similar to that of human hard tissues [1–4]. However, notwithstanding that new bone can form along the surfaces of either porous or dense HAp, the practically medical applications of HAp are still greatly restricted, since HAp is too stable in vivo to be absorbed and substituted by a new bone and the bone conductive effect is thus limited [5–7].

An earlier work by Carlisle [8], which reported that silicon (up to 0.5 wt.%) is often localized in active growth areas (e.g., the osteoid) of the young bone of mice and rats, has demonstrated the importance of silicon for bone formation and calcification. Many of recent investigations on bioactive glasses...
and glass ceramics indicated that apatite layers could form on the surface of those materials after soaking in stimulated body fluid (SBF) and the silanol groups in those materials act as catalysts for the formation of bone-like apatite layers [9–16], which further revealed the significant effect of silicon on bone formation. Seeing that silicon is one of critical elements for the bone regeneration, and that trace element of silicon in calcium phosphate (Ca-P) ceramics or coatings can bring about an evident influence on the biological response as well as crystallographic, mechanical and chemical properties of implant materials [9], several investigators [17–24] have made attempts to elucidate the effect of addition of silicon (Si) or silica (SiO₂) on the sintering behavior of HAp by using different synthetic routes. For instances, over a much wider range of SiO₂ additions in HAp powders fired at 1100°C, Ruys et al. [18] processed Si-substituted HAp using tetraethyl orthosilicate (SiOC₂H₅)₄, TEOS as a silicon source and found an impurity silicocarnotite (Ca₅(PO₄)₂ SiO₄) phase in HAp at the lowest SiO₂ additions accompanied by gradually increasing amounts of α-tricalcium phosphate (α-TCP), β-TCP and a Ca-Si-P-O amorphous phase with increasing content of SiO₂ added. However, based on investigations of Si-substituted HAp similarly using TEOS as the additive, Kim et al. [18, 19] reported that Si-substituted HAp containing 2 wt.% Si keep its original structure intact for the sintering temperatures of up to 1200°C, and the single-phase HAp containing silicon formed with non-existence of extra phases related to silicon oxide or other calcium phosphate species. Another important work has been done by Gibson et al. [20, 21], who adopted silicon acetate (Si(CH₃COOH)₄) as a source of up to 1.6 wt.% silicon and noted that the phase composition remained as HAp with no secondary phases such as TCP or CaO being formed, and no obvious change took place in the symmetry of the HAp crystallographic unit cell but small variations in lattice constants. Quite recently, several investigators [22–26] have studied systematically the preparation, phase composition and phase evolution in the silicon-stabilized tricalcium phosphate/apatite system by firing a stoichiometric HAp precipitate to which silicon was added. A commonly significant finding is that the resultant phase composition included a distinctive phase of silicon stabilized TCP (Si-TCP), which is a novel form of TCP stabilized by the substitution of silicon in tetrahedral phosphorus sites and has a monoclinic structure with the same crystalline space group (P2₁/a) as α-TCP but with characteristically different lattice parameters from α-TCP.

Apparently, all the aforementioned experimental efforts and analyses strongly indicated that the (trace) element of silicon could play an extremely important role in bone regeneration, and that incorporation of silicon into HAp could cause an obvious change in phase structure and composition. In the present study, bioceramic composites of SiO₂-added HAp with different amounts of SiO₂ were produced by sintering directly the mixtures of HAp and silica at 1200°C. The main objective is to reveal the effects of the content of SiO₂ additive on the phase composition and microstructures of such composites and explore the corresponding bone-like apatite layer growth features on the surfaces of these materials in stimulated body fluid (SBF), which is least investigated but is of practical significance for the application of such biocomposites in bone remolding.

2. Experimental

Pure HAp powder (HAP-100, Taihei Chemical Industry Co.) and colloidal silica dispersed in water (Nissan Chemical Industry Co.) were mixed in a ball mill together with ZrO₂ balls and ethanol. After mixing for 24 hrs, the powders were dried and sifted through a 60 mesh sieve. Since the particle diameter of colloidal silica is 10–20 nm, uniformly mixed powders composed of HAp and SiO₂ could be obtained by using this method. In this way, a series of SiO₂-added HAp (HAp-SiO₂) powders containing 0.5, 1.0, 2.0, 5.0 and 10 wt.% SiO₂, respectively, were prepared. After preparation, these powders were calcined at 600°C for 2 hrs.

Disk-shaped pellets of HAp containing different amounts of SiO₂ were produced by pressing uniaxially the processed powders in a 6 mm diameter steel die. The green pellets were sintered at 1200°C for 2 hrs with heating and cooling rates of 100 °C/h. To identify the phase composition and content, X-ray powder diffraction measurements were made on each sintered sample using a Shimadzu XRD-6000S diffractometer. Cu Ka radiation was adopted at the operating condition of 40 kV and 30 mA. The XRD data were obtained over 2θ range of 10–70° at a step size of 0.01°.

After being sintered, one surface of the sample was mechanically ground firstly by #2000 emery paper and then polished by 6 µm diamond paste. Subsequently, the polished samples were thermally etched at 1050°C for 2 hrs or chemically etched in 0.2 M lactic acid for several seconds. Prior to observing the microstructures in a scanning electron microscopy (SEM), the etched surfaces of samples were sputter-coated with a thin electrical conductive layer of gold-palladium alloy to avoid charging in the SEM.

After the sintered samples were mechanically ground by #2000 emery paper, an in vitro bone-like layer growth test was performed by soaking the samples (sample size ~28.3 mm²) at 36.5°C in 30 ml of SBF in polyethylene bottles for 3 days with stirring but without refreshing the solution. The chemical compositions and pH of the SBF (vs. human blood plasma) are given in Table 1. The detailed preparation of SBF was described by Kokubo et al. [27]. After soaking, the features of bone-like layer formed on the sample surfaces were carefully examined by means of SEM.