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Porous biomorphic silicon carbide ceramics coated with hydroxyapatite as prospective materials for bone implants

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ABSTRACT

Porous and cytocompatible silicon carbide (SiC) ceramics derived from wood precursors and coated with bioactive hydroxyapatite (HA) and HA-zirconium dioxide (HA/ZrO_2) composite are materials with promising application in engineering of bone implants due to their excellent mechanical and structural properties. Biomorphic SiC ceramics have been synthesized from wood (Hornbeam, Sapele, Tilia and Pear) using a forced impregnation method. The SiC ceramics have been coated with bioactive HA and HA/ZrO_2 using effective gas detonation deposition approach (GDD). The surface morphology and cytotoxicity of SiC ceramics as well as phase composition and crystallinity of deposited coatings were analyzed. It has been shown that the porosity and pore size of SiC ceramics depend on initial wood source. The XRD and FTIR studies revealed the preservation of crystal structure and phase composition of in the HA coating, while addition of ZrO_2 to the initial HA powder resulted in significant decomposition of the final HA/ZrO_2 coating and formation of other calcium phosphate phases. In turn, NIH 3T3 cells cultured in medium exposed to coated and uncoated SiC ceramics showed high re-cultivation efficiency as well as metabolic activity. The recultivation efficiency of cells was the highest for HA-coated ceramics, whereas HA/ZrO_2 coating improved the recultivation efficiency of cells as compared to uncoated SiC ceramics. The GDD method allowed generating homogeneous HA coatings with no change in calcium to phosphorus ratio. In summary, porous and cytocompatible bio-SiC ceramics with bioactive coatings show a great promise in construction of light, robust, inexpensive and patient-specific bone implants for clinical application.

1. Introduction

A range of materials are currently being tested and developed for applications as medical implants for surgical bone fixation and replacement. Out of these, stainless steel and titanium-based implants are the most commonly used for bone fixation [1,2] while ceramic-based materials are employed for bone substitution [3,4]. Medical implants based on titanium alloys and stainless steel however, possess significantly higher density and Young's modulus than natural bone [5]. This dissimilarity results in stress shielding effects, leading to concentration of stress at the interface between the bone and implant, which could result in reduced stimulation for new bone growth and decreased implant stability [6,7]. Consequentially implant instability requires replacement of the implant thus resulting in undesirable invasive and expensive surgical intervention [8,9]. For this reason, it is critical to develop medical implants with mechanical properties and porosity that match those of human bones and joints.

Synthesis of porous cytocompatible ceramic materials from naturally available and renewable wood sources is an exciting new approach to obtain materials for bone substitution and fixation. This includes synthesis of calcium phosphate-based ceramics, such as hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) [10] and biomorphic silicon carbide (SiC) ceramics [11–13]. It has however been shown that the mechanical properties of human cortical bone, such as tensile strength (90–228 MPa), compression strength (150–260 MPa) and Young's modulus (7.5–25.8 GPa) [14] hardly match those of HA porous ceramics synthesized from wood [15]. On the other hand, it is advantageous to use SiC ceramics synthesized from alternative wood sources, which are porous

Abbreviations: SiC, silicon carbide; CAC, cacodylate; GDD, gas detonation deposition.

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biomorphic materials and mimic the fibrous and porous microstructure of initial wood. Such SiC ceramics possess the mechanical properties (Young's modulus – 20–300 GPa, tensile strength – 150–430 MPa, compression strength – 25–300 MPa) close to those of human cortical bone [11,14,16]. The porosity, pore size and mechanical properties of such ceramics can be varied by changing initial wood source and parameters of synthesis [11,17,18]. The porosity of SiC ceramics (20–90%) is close to the porosity of specific bones in human body (cortical – 5–30%, cancellous – 30–90%) [14,19]. In order to improve cytocompatibility and accelerate bone remodeling, additional coating with bioactive HA and HA/ZrO_2 can be applied. The positive effect of bioglass coating deposited onto SiC ceramics using pulsed laser ablation has been reported, including in vitro and in vivo tests [20,21].

Currently used techniques for deposition of bioactive coatings include plasma spraying, electrophoretic, ion beam assisted and sputter coating approaches. However, most of them often fail to obtain crystalline HA coatings with the required adhesion (ISO standard for HA coating: not less than 15 MPa, [22]). The highest adhesion of HA coating onto titanium-based medical implant could be achieved by plasma-spraying (15–25 MPa), electrophoretic (10–55 MPa), ion beam assisted (40–60 MPa) and sputter coating (80 MPa) approaches [23]. However, these methods have been shown to change crystallinity of HA, forming an amorphous layer between the coating and implant [23-25]. An alternative approach to obtain coatings for biomedical application is to utilize the kinetic energy of detonation of explosive gases, to transport the bioactive powder at high velocities [25]. This effect can be achieved by the gas detonation deposition (GDD) approach. It has been utilized to obtain adhesive and homogeneous coatings from bioactive and bioinert materials, such as HA, tricalcium phosphate (TCP), yttrium stabilized zirconia and bio-glass onto titanium as well as magnesium substrates for bone implant engineering [26,27]. Despite its advantages, this method however has never been applied to introduce bioactive HA-based coatings onto biomorphic SiC ceramics.

Due to the fact that initial wood can be easily processed to create a template with the desired form, the final biomorphic SiC-based implants with bioactive coatings can therefore be customized to meet the patient-specific needs. In this regard, the current study has been performed to analyze the morphology (porosity and pore size distribution) of SiC ceramics synthesized using forced infiltration with liquid silicon of carbon matrices derived from Hornbeam, Sapele, Tilia and Pear wood precursors. In addition, we tested the GDD method to obtain bioactive HA and HA/ZrO_2 coatings onto porous biomorphic SiC ceramics. Moreover, we evaluated the effect of deposition process on the phase composition and crystallinity of deposited coatings, and assessed the cytocompatibility of applied coatings in vitro.

2. Materials and methods

All chemical were purchased from Sigma Aldrich (Germany), unless stated otherwise.

2.1. Synthesis of silicon carbide ceramics

Biomorphic porous SiC ceramics have been synthesized using forced liquid silicon infiltration of carbon matrices derived from different wood precursors (Hornbeam (*Cárpinus*), Sapele (*Entandrophragma cylindricum*), Tilia (*Tilia*) and Pear (*Pýrus*)). This process involved impregnation of carbon matrices by silicon and synthesis of SiC ceramics [11,28]. In the first stage, carbon templates from the wood specimens were prepared. The wood specimens had been previously dried at 90 °C for 15 h. This was performed by wood pyrolysis in the presence of inert argon or nitrogen gas at 900 °C. The second stage was forced infiltration of the carbon matrices with liquid silicon to transform carbon templates into SiC ceramics. This stage was performed in a vacuum by slowly increasing the temperature at a rate of 10–20 °C/min up to 1900 °C. The duration of the second stage was 2 h. The excess carbon has been burn out from the final products in the furnace, in an oxygenated atmosphere at 900 °C for 2 h. The synthesized SiC ceramics samples (length 15 mm, width 10 mm, thickness 8 mm) were used as substrates for HA and HA/ZrO_2 powder deposition.

2.2. Deposition of coatings

HA and HA/ZrO_2 (50% HA/50% ZrO_2, *w*/w) powders were utilized to realize bioactive coatings onto SiC ceramics derived from Pear wood [29]. The HA and HA/ZrO_2 coatings were obtained using the GDD method as described previously [27]. The GDD technology uses energy of explosive gases (propane–butane and oxygen) to transport the powder onto the substrate at high velocities (1200 m/s), thus avoiding excessive overheating during deposition. The GDD method is cyclic and includes the following steps:

1. Feeding of explosive gases to the explosion chamber
2. Transport of powders to explosion chamber
3. Initiation of explosion, formation of detonation wave
4. Transport of powder through a detonation gun to a substrate
5. Expulsion of a chamber and detonation gun with a neutral gas

The process frequency of 6 Hz, powder and gas feeding rates as well as deposition distance of 150 mm were kept constant during deposition.

2.3. Characterization of SiC ceramics and realized coatings

Surface morphology of SiC ceramics as well as deposited coatings was analyzed using a Zeiss Stereo Discovery.V12 microscope (Carl Zeiss Microimaging GmbH, Germany) as well as a scanning electron microscope (SEM, for more details refer to Section 2.6). The images were acquired under different magnifications (20×, 50×, 100×). To analyze

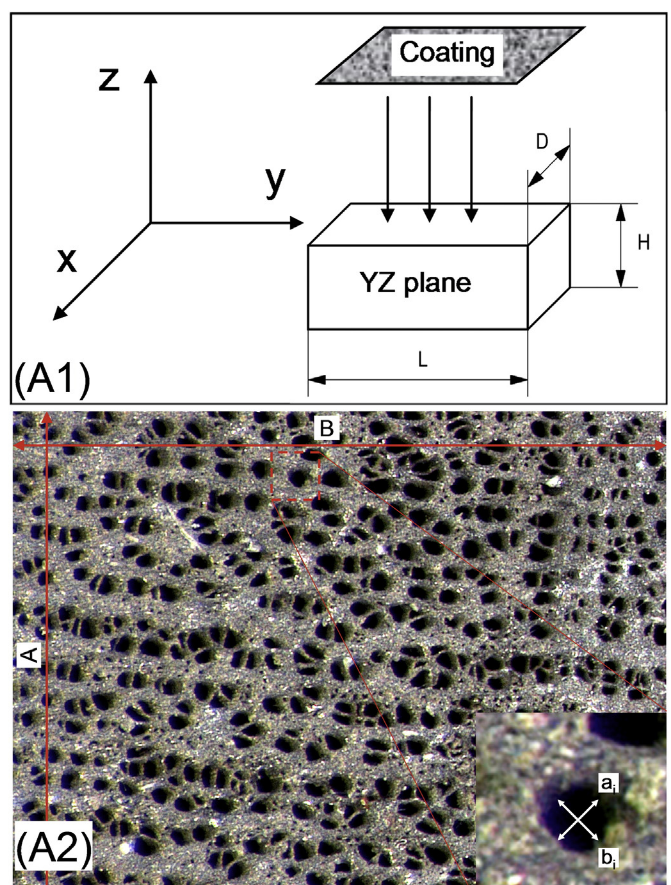

Fig. 1. Strategy of analyzing the pore size and porosity of SiC ceramics.