Aerosol deposition of silicon-substituted hydroxyapatite coatings for biomedical applications

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A B S T R A C T

Silicon-substituted hydroxyapatite (Si-HA) coatings on commercially pure titanium (Ti) were prepared by aerosol deposition using Si-HA powders. Si-HA powders with the chemical formula $Ca_{10}(PO_4)_{6-x}(SiO_4)_x$ $(OH)_{2-x}$, having silicon contents up to $x = 0.5$ (1.4 wt.%), were synthesized by solid-state reaction of $Ca_2P_2O_7$, $CaCO_3$, and SiO_2. The Si-HA powders were characterized by X-ray diffraction (XRD), X-ray fluorescence spectrometry, and Fourier transform infrared spectroscopy. The corresponding coatings were also analyzed by XRD, scanning electron microscopy, and electron probe microanalyzer. The results revealed that a single-phase Si-HA was obtained without any secondary phases such as α- or β-tricalcium phosphate for both the powders and the coatings. The Si-HA coating was about 5 μm thick, had a dense microstructure with no cracks or pores, and showed a high adhesion strength ranging from 28.4 to 32.1 MPa. In addition, the proliferation and alkaline phosphatase activity of MC3T3-E1 preosteoblast cells grown on the Si-HA coatings were significantly higher than those on the bare Ti and pure HA coating. These results revealed the stimulatory effects induced by silicon substitution on the cellular response to the HA coating.

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1. Introduction

Owing to its high affinity to the mineral component of bone, chemical stability and excellent biocompatibility, hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$, HA] is the most popular biomaterial among the entire calcium phosphate family and has been widely used for biomedical applications in a variety of forms such as bulk materials, granules and coatings [1,2]. Especially, the deposition of HA coatings on metallic implants can offer the dual advantages of the metal's high mechanical properties and the ceramic's excellent bioactivity and biocompatibility. Such coatings would be a potential candidate for high load-bearing implant applications in dental implants and orthopedic prosthesis [3,4].

Although synthetic HA has a similar composition to natural bone, it additionally involves some minor ionic substitutions including silicon, magnesium, sodium, and carbonate. These substitutions are reported to play an important role in influencing the biological response by changing the properties of HA such as dissolution rate, crystallinity, and surface chemistry, which has focused increasing research interest on various ion substitutions in HA for enhanced biological performance [5,6].

Since studies by Carlisle suggested that the presence of silicon significantly facilitated bone formation and calcification process [7,8],

silicon has been one of the most important ions associated with HA. Carlisle demonstrated that chicks fed on a silicon-deficient diet showed depressed growth, poor feather development, and bone deformities. Similarly, Schwarz and Milne reported that silicon deficiency in rats changed the skull size and bone structure with a decrease in growth rate [9]. These early reports suggested that silicon would be essential for metabolic processes associated with growth and skeletal development, and that the incorporation of silicon into synthetic HA structure would improve the bioactivity of HA. In this regard, many attempts have been made to develop silicon-substituted HA (Si-HA) [10–12], and recent studies mainly focused on fabricating Si-HA as coatings on metallic implants. Thian et al. developed 1 μm-thick Si-HA coatings with a silicon content up to 4.9 wt.% using magnetron co-sputtering, and in vitro testing revealed that Si-HA coatings exhibited enhanced bioactivity and biofunctionality [13]. Huang et al. showed that Si-HA coatings fabricated using electrostatic spray deposition promoted cell attachment and growth [14]. They suggested that the enhanced dissolution rate of Si-HA with increasing silicon content might exert a stimulatory effect on cell activity in vitro.

Plasma spraying is the only method commercially available for coating metallic implants with HA. However, this technique presents some drawbacks such as low density, poor adhesion to substrate, and phase decomposition due to high-temperature exposure, affecting the long-term stability and life-time of the implant [15]. Therefore, several coating techniques have been proposed to produce HA coatings on metallic implants such as magnetron sputtering [13], biomimetic

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coating [16], pulsed laser deposition [17], and electrophoretic deposition [18]. Among them, magnetron co-sputtering using two targets of silicon and HA has often been applied in recent years to deposit a Si-HA coating on metallic implants, because it can produce dense and high-purity coatings with a controlled stoichiometry [19,20]. However, this technique also has the disadvantages of high facility cost and a relatively low deposition rate of 1.0–1.5 μm/h [21].

In the present study, aerosol deposition (AD) was used as an alternative coating method for Si-HA coating. AD is a deposition technique which can produce a dense and well-adhered ceramic coating at room temperature [22–24]. Because solid powder particles are used as starting materials and the coating is achieved at room temperature, the powder and the resultant coating have the same composition, so that the coating composition can be precisely controlled by changing the powder composition, making it possible to obtain multi-component coatings. Furthermore, AD can produce thin and thick coatings ranging in thickness from submicrometer to several hundred micrometers at a fast deposition rate of more than 5 μm/min [22,23]. These characteristics make AD very suitable for the fabrication of calcium phosphate coatings in biomedical implants and prostheses applications [24].

The aim of this work was to develop and characterize Si-HA coatings formed on titanium (Ti) substrates by AD. We first synthesized single-phase Si-HA powders with a silicon content up to 1.4 wt.% via solid-state reaction and then fabricated Si-HA coatings on the Ti substrates using AD. The physical, chemical and biological properties of the coatings were characterized and the effect of silicon addition on the biological performance of HA coating was investigated.

2. Experimental procedure

2.1. Materials

Si-HA powders containing 0, 0.7 and 1.4 wt.% of Si were synthesized by solid-state reaction method with $Ca_2P_2O_7$, $CaCO_3$ and SiO_2 as starting materials. The calculation of reactant amounts was based on the assumption that SiO_4^{4-} ions would substitute for PO_4^{3-} ions in the HA lattice. The HA and Si-HA powders were prepared with the nominal composition $Ca_{10}(PO_4)_{6-x}(SiO_4)_x(OH)_{2-x}$ ($x = 0$, 0.25 and 0.5). The calcium pyrophosphate $Ca_2P_2O_7$ was obtained by heating $CaHPO_4$ (SDBNI Co., Ltd., Ansan, Korea) at 700 °C for 10 h. Commercial $CaCO_3$ (Wako Pure Chemical Industries Ltd., Osaka, Japan) and SiO_2 (Aldrich Chemical Co., Milwaukee, USA) powders were used. According to Table 1, appropriate amounts of starting materials were weighed, mixed and further milled using zirconia balls in a ball mill for 30 h with distilled water. The mixed slurries were then dried in a rotary evaporator and heat-treated at 1100 °C for 20 h under air atmosphere. The heated powders were used for the AD fabrication of the coatings.

2.2. Aerosol deposition (AD)

The coating was deposited on Ti substrate by AD. Prior to coating, a 0.5 mm thick sheet of commercially available pure titanium (CP-Ti, JIS Grade 2) was cut into two types of small pieces for use as the substrate. Disk-type Ti substrates with a diameter of 25 mm and a thickness of 0.5 mm were used for adhesion strength test of the coatings. For the other characterizations including phase analysis, microstructural observation and in vitro cell tests, square-type Ti

substrates with a size of 10 mm × 10 mm were used. The substrates were ground with 2000 grit SiC paper and ultrasonically rinsed in distilled water and acetone.

Full details of the equipment utilized in the AD system have been described elsewhere [22]. The powder mixed with a carrier gas in aerosol chamber was ejected onto the Ti plate set in deposition chamber through a slit-type nozzle with a 10×0.5 mm^2 rectangular opening. A dense coating layer was formed by the collision of accelerated powder particles with the Ti plate. The flow rate of air as the carrier gas was 30 l/min. The 5 μm-thick coatings were deposited over the entire surface of the Ti plates by scanning the Ti plates on the motorized X–Y stage at a scanning speed of 1 mm/s.

2.3. Characterization

HA and Si-HA powders used for AD were characterized by a laser diffraction particle size analyzer (HELOS/BF, Sympatec GmbH, Clausthal-Zellerfeld, Germany) and a scanning electron microscope (SEM, JSM-5800, Jeol Co., Tokyo, Japan). The crystalline phases of the powders and the coatings were examined by an X-ray diffractometer (XRD, D-MAX 2200, Rigaku Co., Tokyo, Japan) using monochroma-tized CuK$_\alpha$ radiation at 36 kV and 26 mA. The synthesized powders underwent quantitative elemental analysis by X-ray fluorescence spectrometry (XRF, PW2400, Philips Ltd., Netherlands). Fourier transform infrared (FT-IR) spectra were obtained using a Bruker IFS88 FT-IR spectrometer. The elemental composition of the coatings was determined by an electron probe microanalyzer (EPMA, EPMA-1600, Shimadzu, Kyoto, Japan).

SEM was used to observe the surface and cross-sectional morphologies of the coatings at an accelerating voltage of 20 kV. The surface roughness of the coatings was measured by means of a laser surface profilometer (Perthometer PGK 120, Mahr GmbH, Göttingen, Germany). The surface parameter used to evaluate the surface roughness was the arithmetic average roughness (R_a).

The tensile adhesion strength between the coating and substrate was measured using a universal testing machine (Instron series IX automated materials testing system, Instron Corp., MA, USA) according to the standard adhesion test (ISO 13779-4) [25]. Five replicates of each sample were tested. The coatings were deposited on a Ti substrate as circles with a diameter of 25 mm and a thickness of 0.5 mm, and the fixtures were bonded on the coating's top side and the substrate's bottom side with thermal cure, high strength epoxy (3M Scotch-Weld Epoxy Adhesive 2214, 3 M Corp., St. Paul, MN) and then cured at 170 °C for 24 h. In tensile testing, the fixtures were pulled in the opposite directions at a cross-head speed of 1 mm/min until the coating failure. The adhesion strength value was obtained from the load at which failure of the coating occurred. The average values and standard deviation for adhesion strength measurements are presented.

2.4. In vitro cell studies

MC3T3-E1 preosteoblast cells (CRL-2593, ATCC, Manassas, VA, USA) were used to assess the biological response of the Si-HA coatings. These cells were cultured in α-minimum essential medium (α-MEM, Join Bio Innovation, Seoul, Korea) supplemented with 10% heat-inactivated fetal bovine serum (GIBCO, USA), 2 mM L-glutamine, 50 IU ml^{-1} of penicillin,

Table 1
Quantities of reactants, the expected wt.% of Si, molar ratios, and chemical formula.

	Si (wt.%)	$Ca_2P_2O_7$ (mol)	$CaCO_3$ (mol)	SiO_2 (mol)	Ca/P (molar ratio)	$Ca_{10}(PO_4)_{6-x}(SiO_4)_x(OH)_{2-x}$
HA ($x = 0$)	0	3	4	0	1.67	$Ca_{10}(PO_4)_6(OH)_2$
0.7 wt.% Si-HA ($x = 0.25$)	0.7	2.875	4.25	0.25	1.74	$Ca_{10}(PO_4)_{5.75}(SiO_4)_{0.25}(OH)_{1.75}$
1.4 wt.% Si-HA ($x = 0.5$)	1.4	2.75	4.5	0.5	1.82	$Ca_{10}(PO_4)_{5.5}(SiO_4)_{0.5}(OH)_{1.5}$