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Mechanical and in vitro biological performances of hydroxyapatite–carbon nanotube composite coatings deposited on Ti by aerosol deposition

Byung-Dong Hahn [a], Jung-Min Lee [a], Dong-Soo Park [a,*], Jong-Jin Choi [a], Jungho Ryu [a], Woon-Ha Yoon [a], Byoung-Kuk Lee [a], Du-Sik Shin [b], Hyoun-Ee Kim [b]

[a] *Functional Ceramics Group, Functional Materials Division, Korea Institute of Materials Science (KIMS), 66 Sangnam-Dong, Changwon, Gyeong-Nam 641-010, Republic of Korea*

[b] *School of Materials Science and Engineering, Seoul National University, San 56-1 Sillim-Dong, Gwanak-gu, Seoul 151-742, Republic of Korea*

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Abstract

Hydroxyapatite (HA)–carbon nanotube (CNT) composite coatings on Ti plate, produced by aerosol deposition using HA–CNT powders, were developed for biomedical applications. For the deposition process HA–CNT powder mixtures with CNT contents of 1 and 3 wt.% were used. Dense coatings with a thickness of 5 μm were fabricated, irrespective of the content of CNTs. No pores or microcracks were observed in the coatings. The coatings had good adhesion to the substrate, exhibiting a high adhesion strength, ranging from 27.3 to 29.0 MPa. Microstructural observation using field-emission gun scanning electron microscopy and transmission electron microscopy showed that CNTs with a typical tubular structure were found in the HA–CNT composite coatings. Nanoindentation tests revealed that the mechanical properties, such as the hardness and elastic modulus, were significantly improved by the addition of the CNTs to the HA coating. In addition, the proliferation and alkaline phosphatase (ALP) activity of MC3T3-E1 pre-osteoblast cells grown on the HA–CNT composite coatings were higher than those on the bare Ti and pure HA coating. The ALP activity of the composite coatings considerably improved as the CNT content increased. These results suggest that CNTs would be an effective reinforcing agent to enhance both the mechanical and biological performances of HA coatings.

Keywords: Hydroxyapatite; Carbon nanotube; Aerosol deposition; Nanoindentation; Biological performance

1. Introduction

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HA), which belongs to the class of calcium phosphate-based biomaterials, has been widely used for a variety of biomedical applications in dentistry and orthopedics, due to its chemical resemblance to the mineral component of bone, excellent biocompatibility and osteoconductivity [1–3]. However, the peculiar brittleness and low fracture toughness of HA have restricted its usage in applications such as high load-bearing implants [4]. One way to overcome this problem is to coat HA on a metallic implant surface. The HA-coated implant can combine the high mechanical strength of the metal with the excellent biocompatibility and bioactivity of the ceramic and is therefore suitable for implants in high load-bearing applications [5,6].

Recently, in order to improve the mechanical properties of the HA coating itself, HA composite coatings in which HA is combined with other materials used as a second phase, such as ethylene-based polymer [7], yttria-stabilized zirconia [8] and alumina [9], have been extensively studied. However, considerable amounts of the second phase are required for a significant improvement in the mechanical properties of the composite coatings. Moreover, the bioinertness or poor bio-

* Corresponding author. Tel.: +82 55 280 3345.
E-mail addresses: pds1590@kims.re.kr, jh980214@hotmail.com (D.-S. Park).

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activity of these phases often results in the HA composite coatings having much lower biological properties than HA itself [8]. Therefore, for the fabrication of composite coatings having good mechanical properties without any deterioration in their bioactivity it is necessary to use a second phase with high bioactivity or to keep the amount of the second phase as low as possible, so as not to lower the biological performance of the coatings significantly.

Carbon nanotubes (CNTs), which were first discovered by Iijima in 1991 [10], have been widely investigated owing to their excellent thermal, electrical and mechanical properties resulting from their unique atomic structure [11,12]. CNTs consist of a rolled-up sheet of graphite and generally exhibit a high aspect ratio in the range of 1000–10,000. It was reported that CNTs exhibit a remarkable elastic modulus of more than 1 TPa and tensile strength reaching 30 GPa [13,14]. These excellent mechanical properties of CNTs have stimulated their use as a reinforcing agent for high strength composites [15,16].

Since the bioactivity of CNTs was reported [17–19] their use in biomedical applications has been anticipated. The combination of biological and excellent mechanical properties of CNTs has opened a new research field of CNT reinforced HA composite coatings [20,21]. Balani et al. fabricated an HA–CNT composite coating using plasma spraying and reported that its fracture toughness was improved by 56% compared with that of a monolithic HA coating [20]. Although plasma spraying is the most popular method in commercial use to produce HA coatings on implants, plasma sprayed HA coatings have several disadvantages, such as their low density, susceptibility to microcracks and phase decomposition on high temperature exposure, thereby limiting the long-term stability of the implant [22]. Another reported method of producing HA–CNT composite coatings is electrophoretic deposition, which is known to be a low cost and simple method of producing HA coatings on metallic implants [23]. Kaya et al. investigated the mechanical properties of an electrophoretically deposited HA–2 wt.% CNT coating and reported that it showed a 400% improvement in adhesion strength over a monolithic HA coating [21]. However, the adhesion strength value of the HA–CNT composite coating was as low as 2.8 MPa, which might make it unsuitable for real applications.

Aerosol deposition (AD) is a newly developed coating method which is capable of depositing dense coating layers on various substrates such as metals, ceramics and plastics [24,25]. This technique uses solid particles as the starting materials and the coating layer is formed by the collision of the particles with a substrate. AD has received considerable attention due to its low processing temperature (near room temperature), high adhesion strength and precise control of the coating composition, making it very suitable for producing HA coatings for use in biomedical applications.

In the present work we deposited HA–CNT composite coatings on Ti substrates using AD with the aim of improving the mechanical and biological properties of HA coatings. For the coating process a powder mixture of HA and well-dispersed CNT was prepared. The mechanical properties of the coatings were measured using nanoindentation as a function of the amount of CNTs added to the coatings. The in vitro biological properties of the coatings were also evaluated in terms of cell proliferation and differentiation.

2. Experimental procedure

2.1. Materials

A commercially available nanocrystalline HA (Samjo Industrial Co. Ltd, Cheongwon, Korea) powder with an average particle diameter of about 15 nm was used as the starting material. The as received HA powder was heated at 1100 °C for 2 h in order to obtain a powder with a particle size appropriate for coating. In addition, commercially available multi-walled CNT (CM-95, Hanwha Nanotech Co. Ltd, Seoul, Korea) with a diameter of 10–15 nm and length of 10–20 μm was also used for fabricating the HA–CNT composite coatings by AD.

Since CNTs tend to agglomerate due to the strong van der Waals attractions between them they must be dispersed uniformly within the HA matrix for them to act as an effective reinforcement in HA–CNT composite coatings. The dispersion technique used in this study was acid treatment, which introduced COOH groups on the surface of the CNTs by chemical oxidation, resulting in good dispersion of the CNTs in the solvent [26]. The CNTs were refluxed in an acid solution of H_2SO_4 and HNO_3 (1:3 by volume) at 130 °C for 30 min, following by washing to pH 7 using distilled water. The acid-treated CNTs were then added to an aqueous suspension of the dispersed HA powder and ultrasonically mixed for 2 h. The concentrations of CNTs added to the HA suspension were 1 and 3 wt.% in this study. After drying the HA–CNT powder mixtures were prepared for the composite coating. They were called, respectively, HA–1 wt.% CNT and HA–3 wt.% CNT.

2.2. Preparation of HA coating

The HA–CNT composite coating was deposited at room temperature using AD. Full details of the apparatus utilized in the AD system have been described elsewhere [24]. The substrates used for the coating deposition were commercially pure Ti plates with dimensions of $10 \times 10 \times 0.5$ mm. The Ti plates were rinsed in distilled water and ultrasonically washed in acetone for 10 min before coating. A slit-type nozzle with a 10×0.5 mm^2 rectangular opening was employed and the flow rate of air used as a carrier gas was 30 l min^{-1}. Coatings with a thickness of 5 μm were deposited over the entire surface of the Ti plates by scanning the Ti plates on a motorized X–Y stage for 1 min.

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