Fabrication of Nano-structured HA/CNT Coatings on Ti6Al4V by Electrophoretic Deposition for Biomedical Applications

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Abstract

In order to improve the bone bioactivity and osteointegration of metallic implants, hydroxyapatite (HA) is often coated on their surface so that a real bond with the surrounding bone tissue can be formed. In the present study, cathodic electrophoretic deposition (EPD) has been attempted for depositing nanostructured HA coatings on titanium alloy Ti6AI4V followed by sintering at 800 ^{o}C. Nano-sized HA powder was used in the EPD process to produce dense coatings. Moreover, multi-walled carbon nanotubes (CNTs) were also used to reinforce the HA coating for enhancing its mechanical strength. The surface morphology, compositions and microstructure of the monolithic coating of HA and composite coatings of HA with different CNT contents (5 to 20%) on Ti6AI4V were investigated by scanning electron microscopy, energy-dispersive X-ray spectroscopy and X-ray diffractometry, respectively. Electrochemical corrosion behavior of the various coatings in Hanks' solution at 37°C was investigated by means of open-circuit potential measurement and cyclic potentiodynamic polarization tests. Surface hardness, adhesion strength and bone bioactivity of the coatings were also studied. The HA and HA/CNT coated Ti6AI4V had a thickness of about 10 μm without cracks, with corrosion resistance higher than that of the substrate and adhesion strength higher than that of plasma sprayed HA coating. The properties of the composite coatings were optimized by varying the CNT contents. The enhanced properties could be attributed to the use of nano-sized HA particles and CNTs. Compared with the monolithic HA coating, the CNT-reinforced HA coating markedly increased the coating hardness without deteriorating the corrosion resistance or adhesion strength.

I. Introduction

As the global population increases in age, there is a parallel increase in the demand of medical implants. The worldwide sales of orthopedic implants alone in 2003 was $8.7 billion and projected to increase at an annual growth rate of 12.5% to reach $17.9 billion in 2009 [1]. It is important to understand the characteristics of implant materials interacting with physiological environment such as bio-corrosion, bioactivity and osteointegration. Titanium (Ti) alloys are commonly employed as orthopedic and dental implants because of their excellent corrosion resistance and high mechanical strength. The oxide layer formed spontaneously on the surface of these alloys makes them very stable. This oxide layer reforms instantly when it is removed or destroyed by mechanical means. Nevertheless, they are susceptible to corrosive attack by body fluids with subsequent release of metallic ions which might cause adverse effects to the surrounding tissues. Moreover, metallic surfaces are not bone bioactive, thus leading to poor osteointegration. In order to increase the bone bioactivity of metallic implants, hydroxyapatite [Ca_{10} $(PO)_6(OH)_2$, HA], a bioceramic which resembles the mineral constituents of human bones and teeth, is often coated on their surface. Plasma spraying of HA coatings is currently the only commercial process in use but long-term stability of plasma sprayed coatings could be a problem because of their high degree of porosities, poor bond strength, non-stoichiometric composition, non-uniformity and amorphous structure [2-4]. In view of these shortages, electrophoretic deposition (EPD) has been attempted for fabricating HA coating with advantages including short formation time, simplicity in instrumentation, and capability of coating complex-shaped implants [5]. It has been reported that nano-structured coatings fabricated by EPD have high chemical homogeneity, reduced flaw size and microstructural uniformity, and require a sintering temperature of at least 800 ^{o}C for densification [6-7]. The nano-sized grains and the high volume fraction of grain boundaries in nano-structured HA can increase osteoblasts adhesion, proliferation, and mineralization [8]. CNTs possess unique mechanical properties. However, there has been only limited work on incorporating CNTs in bioceramic coatings for biomedical applications [9]. The aim of the present work is to utilize cathodic EPD followed by sintering for fabricating bioactive monolithic HA and HA/CNT coatings on Ti6AI4V. The surface characterization, corrosion behavior and apatite-forming ability of the HA and HA/CNT coated Ti6AI4V specimens will be investigated.

II. Results

Commercial needle-shaped nano-HA powder with size of 50 nm x 200 nm was used as the coating material. As-received titanium alloy Ti6AI4V in the form of circular bar with a diameter of 13 mm was cut into discs with thickness of 5 mm as the substrate. The discs were mechanically ground with 800-grit silicon carbide paper, washed thoroughly with water, degreased with ethanol in an ultrasonic bath, and then allowed to dry in air for the EPD process. The HA powders (2.5 wt%) was added to ethanol and mixed by a magnetic stirrer for 10 minutes. The powder was dispersed ultrasonically to obtain a homogeneous colloidal suspension. Multi-walled CNT powder with an average tube diameter of 30 nm and length of 1 Pm was added to the suspension of HA powder (in ratio of 1:20 to 1:4 by wt.) and ultrasonically mixed for 30 minutes. The EPD process was conducted at a DC voltage of 200 V for 20 seconds at 25 ^{o}C. After EPD, the HA and HA/CNT coated specimens were allowed to dry in air at room temperature for 24 hours and then sintered in a vacuum furnace at 800 ^{o}C and 5 Torr, at a heating rate of 100 ^{o}C/h, a dwell time of 1 h, and a cooling rate of 100^{o}C/h.

Figs 1 and 2 show the SEM micrographs of HA-coated and HA/20%CNT-coated Ti6AI4V. After sintering, the EPD HA and HA/CNT coatings possess good integrity without micro-crack due to the use of nano-sized HA particles and CNTs, which resulted in good packing. Thermal effect was minimized because low sintering temperature was used. The polarization curves of Ti6AI4V without and with coatings in Hanks' solution at 37 ^{o}C (Fig. 3), both HA-coated and HA/CNT-coated Ti6AI4V significantly shifted to lower current density, showing higher corrosion resistance. In addition, the hardness of the HA-coated and HA/CNT coated Ti6AI4V was improved by 1.6 and 3.2 times, respectively. Furthermore, compared with Ti6AI4V, the bone bioactivity of the coatings was also found to be enhanced.

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Figure 1 - SEM micrograph of HA-coated Ti6l4V

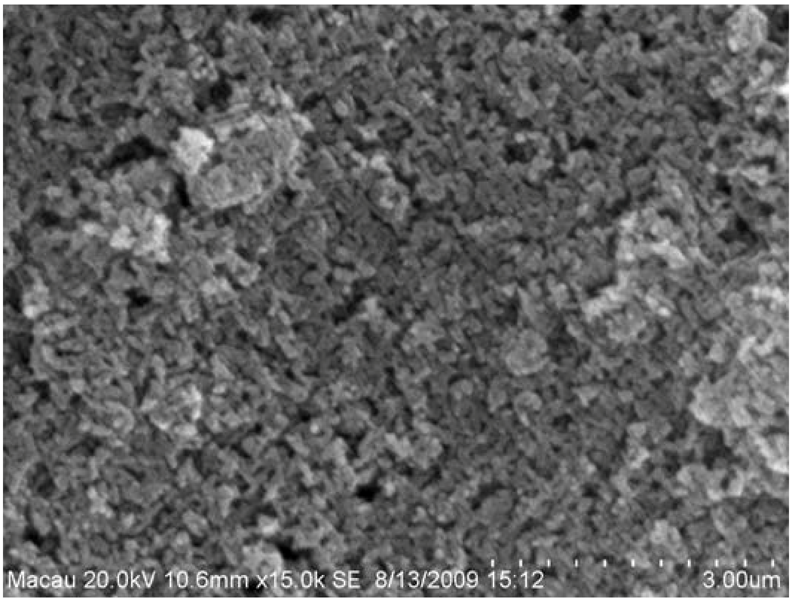

Figure 2 - SEM micrograph of HA/20%CNT-coated Ti6Al4V

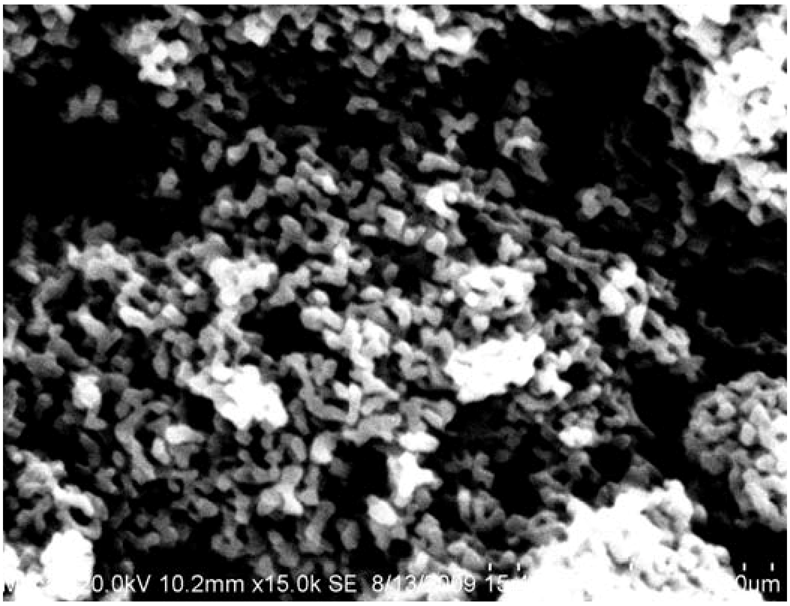

Figure 3 – Polarization Curves of Ti6Al4V, HA-coated Ti6Al4V and HA/20%CNT-coated Ti6Al4V in Hanks' solution at 37ºC