Nano-mechanical testing of novel bioactive carbon nanotubes/HAP nano particles composite coating

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ABSTRACT

Hydroxyapatite (HAP) is an important material for biomedical implants, as its chemical composition is similar to that of bone tissue.
Compared with human cortical bone, however, HAP has poor mechanical properties and lower fracture toughness. Therefore, it would be desirable to develop bioactive nano composite materials with mechanical properties more closely related to living bone.
In the present study, high quality multi wall carbon nanotube (CNT) reinforced HAP nano particle composite coatings have been successfully deposited on the surface of a Ti alloy substrate using electrophoretic deposition. The resulting nano-composite materials showed good dispersion and homogeneous distribution of carbon nanotubes in HAP nanoparticles coating.
Nano-mechanical properties (e.g., hardness and elastic modulus), adhesion, the deformation and damage behaviours of this potential implant material were evaluated using nano-indentation and nano-scratch techniques.

Keywords: nano-particles, coatings, nano-indentation

1. INTRODUCTION

Bone itself is an organic-inorganic composite and it is logical that the search for a new generation of implant materials should focus on hybrid materials that combine the strength and stiffness of an inorganic compound with the flexibility, toughness and resorbability of an organic phase. The objective of this work was to use hydroxyapatite (HAP), a calcium phosphate that is closely related to the mineral component of bone and to reinforce it with carbon nanotubes (CNTs), a material recently used in many biological/orthopaedic applications [1-2]. Carbon nanotubes (CNTs) with their high aspect ration and excellent mechanical properties, have the potential to strengthen and toughen these HAP without offsetting their bioactivity, thus opening up a wider range of possible clinical uses for the materials [3-4] The goal of our work was to develop a simple processing route that allowed us to fabricate coatings with a controlled microstructure such that the factors affecting the mechanical properties (proportion of the components, particle size and shape of the inorganic phase etc.) could be explored systematically. Several studies have examined the effect of incorporating CNTs with various ceramics to improve mechanical properties [5-6]. However, recently very little work has been done on the effect CNTs have on the mechanical properties of HAP nanoparticles.

In this study, a novel approach has been used to produce nano-bio-composite coatings of HAP with CNT additions between 0 and 5 wt% at a room temperature. An electrophoretic deposition technique was used to deposit the nano-bio composite coatings. The electrophoretic deposition as a method for fabrication of ceramic coatings [7-13] has attracted increasing attention due to its advantages over alternative coatings on complex shaped substrates, the simplicity of the process, low cost equipment and high deposition rate .The aim was to find a loading level of CNTs that would be expected to improve the mechanical strength of novel implant materials without deteriorating the biocompatibile properties of HAP.
The effects of the concentration of the CNTs on the mechanical properties of the composite coatings have been determined.

The adhesion strength of the nano-structured HAP-CNTs nano-composite coatings were evaluated using Nano-indentation and nano-scratch technique.

2. EXPERIMENTAL PROCEDURES

2.1 Preparation of HAP/carbon nanotubes (CNTs) suspensions and its coatings on Ti

The hydroxyapatite nano powder was prepared using a Sol-gel technique with phosphoric pentaoxide (P_2O_5) and calcium nitrate tetrahydrate (Ca $(NO3)_2.4H_2O$) as reported previously [14].
Synthesised hydroxyapatite spherical nano powders (Fig1a) with an average particles size ranging from 20 to 50nm and commercially multiwalled carbon nanotubes (CNTs) with a diameter from 20-40nm were selected as the starting precursor materials for fabricating the carbon nanotube (CNT) reinforced hydroxyapatite composite coatings. The HAP nano particle suspensions were mixed in three different weight proportions, namely 0%, 1% and 5% CNTs in ethanol. Cetyltrimethul ammonium bromide (CTAB) (0.1M) was used as a dispersion agent at a concentration of 0.5 wt%. The mixture was sonicated for 2 hours to thoroughly disperse the mixture powders, and then suspension was then stirred at room temperature for 2 hours.
The substrate used for coating was Ti-6Al-4V with dimension size of 25x10x1mm.
The EPD was carried out by applying an electric field between stainless steel electrodes (as cathode) and a substrate (anode). The applied voltage, deposition time and suspension concentration were the parameters chosen to be varied in order to optimize the coating quality by a systematic approach. The parameters were varied initially over a wide range to gain knowledge about the influence of each parameter on the reproducibility of the EPD process.

The parameters were than optimized with the aim of improving the coating quality. The applied voltage was between 5 to 30 volts. The distance between the electrodes was kept constant during all of the experiments at 15mm. The deposition time was varied between 2 min and 10 min. The suspensions were prepared with HAP nano powders mixed with 1 and 5wt% CNTs. The green coatings were dried at room temperature for 24h before they were sintered in N_2 at 800ºC for 2h.

2.2 Characterization

The morphologies of the synthesised HAP nano particle and HAP-CNTs dispersions were observed by scanning electron microscopy (SEM). The samples were investigated with SEM (JEOL JSM-840) and Zeiss supra SEM equipped with an EDX system. The sample powders were made by suspension method, mounted on Al stubs and gold coated before subjecting of SEM analysis. The microstructures of the HAP/CNTs composite coatings were examined by SEM, after vapour deposition of conductive gold layer on the surface of HAP deposit.

The Nanoindentation test were carried out using the Nano-test 600 (Micro-materials Limited, UK) instrument at 25˚C. A three-sided pyramidal Berkovich indenter was used. The load and displacement data were obtained and the elastic modulus, E, and the hardness values, H, of the coatings were determined.

The nano-scratch tests were performed using the multipass scratch test mode with a conical indenter (Rockwell type, 120 diamond cone) topped with a spherical end of 25um in radius. During the test, the specimen was moved against the conical indenter at a speed of 100nm/s for a total length of 1000µm. After an initial 300µm pre-scan under a small load of 1mN, the testing load was applied to the indenter. Testing was conducted in a multipass test mode under linear loading. Loads of 50, 150 and 300mN were selected for the scratch testing. For a linear loading scratch, the load was increased progressively from 1mN to the maximum selected load. For each scratch test, a surface profile along the track was measured.

The failure mode of scratch track was examined by SEM and atomic Force microscopy (AFM, Digital Instruments Nanoscope).

3. RESULTS AND DISCUSSION

Figures 1b and c show the SEM micrographs of HAP/CNT suspensions at different concentrations of CNTs that confirm a uniform distribution of CNTs and HAP particles. Fig.2 shows typical digital micrographs of HAP nanoparticles and HAP/CNTs nano composite coated Ti alloy obtained by electrophoretic deposition. The SEM analysis of composite coatings with the powders mixture of HAP-1wt%CNT and HAP-5wt%CNT, after heat treatment at 800ºC for 2h in N_2 at the low magnification of both samples shows fairly homogenous and thin coatings that were uniform throughout the complete length of the foil (Figs 3a and c). A homogenous and controlled deposition of HAP-CNTs mixture on Ti alloy foil can, therefore, be confirmed for 15 volts voltage and 2min deposition time. An increase in the deposition time resulted in an increased coating thickness that resulted cracking on the coating. The SEM micrograph in Figure 3d shows the good dispersion and mechanical interlocking between HAP nanoparticles and CNTs with some instances of agglomeration and the presence of voids being observed.

The SEM micrograph in Fig 3b shows that CNTs are uniformly distributed in the coating without agglomeration. Retention and distribution of CNTs is critical since CNTs provide for the enhanced strength and fracture toughness of the HAP. It must be mentioned that voids is critical in allowing the growth of cells because surfaces influence the protein interaction leading to subsequent cell adhesion.

3.1 Nano-indentation testing

Nano-indentation testing was performed in a load-controlled mode. The area function for the Berkovich diamond indenter was determined by indentations into fused silica from 0.5 to 200mN. The coated sample used for nano-indentation was plate shaped with a dimension size 50x25x1mm (Fig 2). Pure HAP nano particles coating heat-treated at 800C for 2h was also tested for comparison. The data were analyzed with the Oliver and pharr[15] method and five repeat load partial unload experiment were performed on each sample. Fig 4 shows the typical load displacement curves for HAP, HAP-1wt%CNT and HAP-5wt%CNT coatings, respectively. As can be seen, the HAP-5wt%CNT coating was more resistant to the penetration by the indenter than the HAP and HAP-1wt%CNT coatings. The average hardness and elastic modulus for these composite coatings are indicated in table 1. It shows that both hardness and elastic modulus increase with the addition of CNT content. It is clearly seen that the addition of CNTs has no strong effect on the value of modulus of these coatings, but it has notable effect on the value of hardness of these composite coatings. The reason for this phenomenon might be the multiwalled CNTs usually has structural defects, which can result in the notable decrease of the value of the modulus [16]. This characteristic may be attributable to the variations of the coating microstructures and thus the mechanical properties caused by different coating thickness growth rate during the deposition process.

3.2 Nano-scratch testing

Fig.5 shows the typical scratch traces under different loadings for HAP-5wt%CNT nano composite coatings. Fig 5a is a nano scratch test result at 150mN and shows that no wear occurs at this low load. As the applied load was increased, a dramatic failure event finally observed at 350µm (corresponding to 350mN) .The displacement of the scratch profile (Fig. 5b) indicated the damage of the coating. This is further confirmed by SEM examination (Fig 6b). The scratch load at this point can therefore be taken as the critical load (Lc) for the coating failure. Fig. 6a shows the nano scratch track of a HAP-5wt%CNT coating examined under AFM. It was evident from this that there was a certain amount of material removal during the scratch test. AFM also revealed the formation of material pile-up along the sides of the scratch track. The relatively large failure areas related with dense microstructure and good mechanical interlocking between HAP nano-particles and CNTs confirmed that coating/substrate interface was quite strong. Similar behaviour was observed on the HAP-1wt%CNT composite coating, except that the critical loads

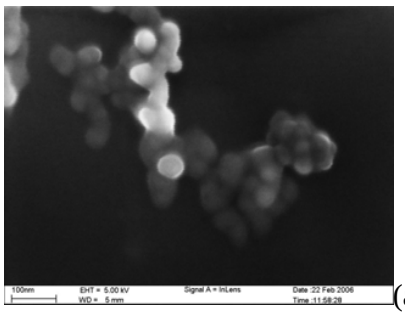
occur at lower load. Failures were less extreme on this coating.

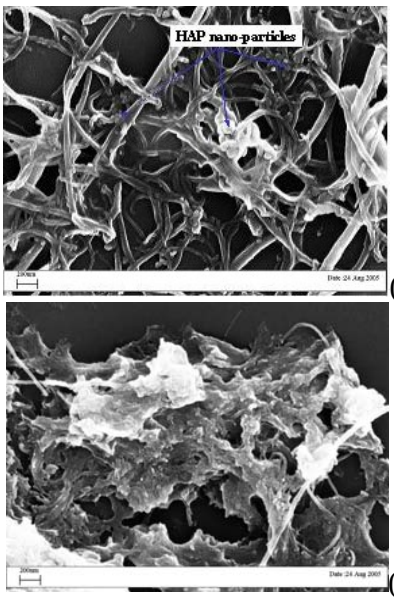
4. CONCLUSION

- Nano-sized spherical HAP particles were successfully incorporated into the CNTs
- In this paper, novel carbon nanotube (CNT) reinforced hudroxyapatite (HAP) nano particle nano-bio-composite coatings have been successfully deposits on the surface of a Ti alloy substrate using EPD.
- The nano-bio-active composite coatings were highly dense and possessed excellent microstructural homogeneity as well good interfacial properties. The thickness for a high integrity coating 1μm was obtained in 4min, at the optimal applied potential of 30V.
- Nano-indentation test shows that the hardness and modulus increased with an increase the content of CNTs.
- The nano-scratch test provided a valuable additional test procedure to evaluate the adhesion of the coating to the substrate. This test method will be useful for the future development of advanced nano-structured biomaterials coatings
- The adhesion of the nano composite coatings was higher compared to that of the pure HAP nano-particles coatings.
- The linearly increasing load mode of nano-scratch test was found the most effective and informative test for determining the critical load (Lc) for nano-mechanical test results coating failure.
- The results suggest that the newly developed HAP/CNTs nano bio-composite coatings may be superior for bone tissue engineering.
- Nano-mechanical test results demonstrated the effects of the microstructure properties of the nano-composite coatings.

Table1

Properties	HAP	HAP-1wt%CNTs	HAP-5wt%CNTs
Hardness (GPa)	2.8	6.0	7.12
Elastic modulus(GPa)	150	155	160


(a)

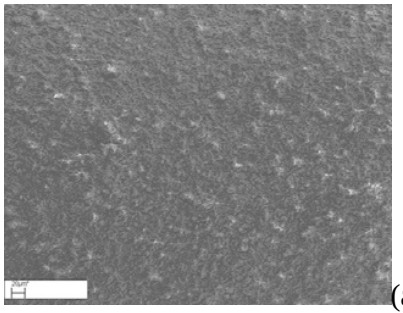


(b) (c)

Figure 1 SEM micrographs, (a) HAP nano-partilces, (b) HAP- 5wt% CNTs suspension, (c) 1wt% CNTs


(a) (b)

Figure 2 Micrographs of Ti alloy coated foils, (a) HAP-5wt%CNTs (b) HAP-0wt%CNTs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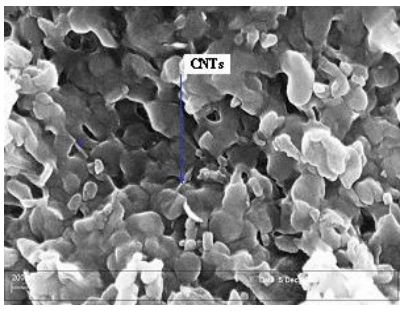

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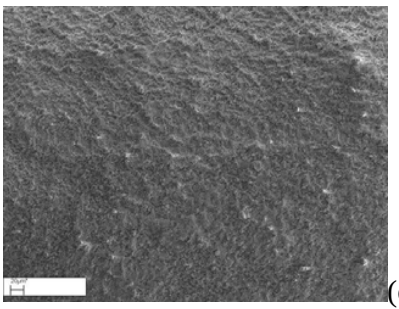
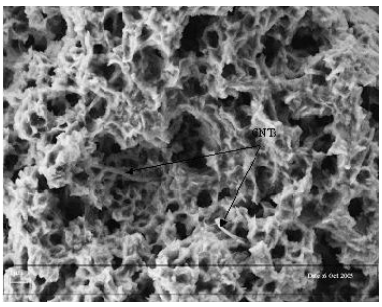


(c)



(d)

Figure 3 SEM micrographs of Ti alloy coated,(a) HAP-1%CNTs, (b)HAP-5%CNTs

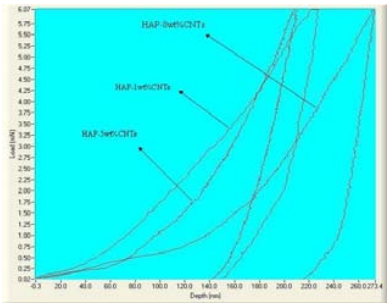
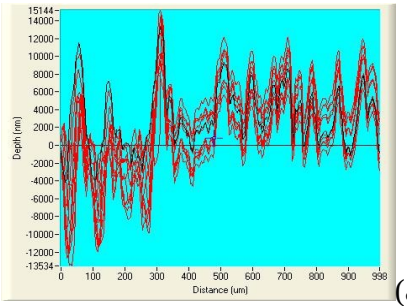
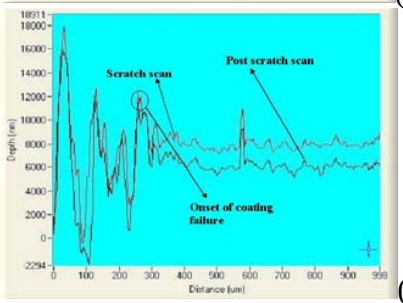


Figure 4 Nanoindentation load -displacement curves

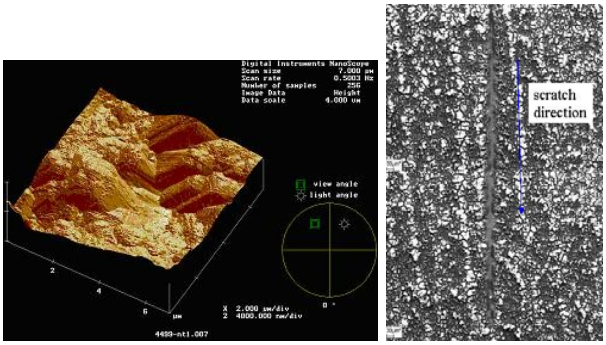


(a)



(b)

Figure 5 (a) Nano-scratch curves of HAP-5wt%CNT composite coating, (a) 150mN, (b) 300mn



(a) (b)

Figure 6 (a) AFM image showing the surface of scratch track of HA-5wt%CNTs composite coating,(b) SEM scratch track

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