Materials Science and Engineering C 70 (2017) 805–811

Contents lists available at ScienceDirect

Materials Science and Engineering C

journal homepage: www.elsevier.com/locate/msec

Preparation and properties of in-situ growth of carbon nanotubes reinforced hydroxyapatite coating for carbon/carbon composites

Shoujie Liu, Hejun Li *, Yangyang Su, Qian Guo, Leilei Zhang *

State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, Xi'an 710072, China

ARTICLE INFO

Article history:
Received 22 June 2016
Received in revised form 11 August 2016
Accepted 26 September 2016
Available online 28 September 2016

Keywords:
Hydroxyapatite coating
In-situ growth of carbon nanotubes
Adhesion strength
Corrosion
Biocompatibility

ABSTRACT

Carbon nanotubes (CNTs) possess excellent mechanical properties for their role playing in reinforcement as imparting strength to brittle hydroxyapatite (HA) bioceramic coating. However, there are few reports relating to the in-situ grown carbon nanotubes reinforced hydroxyapatite (CNTs-HA) coating. Here we demonstrate the potential application in reinforcing biomaterials by an attempt to use in-situ grown of CNTs strengthen HA coating, using a combined method composited of injection chemical vapor deposition (ICVD) and pulsed electrodeposition. The microstructure, phases and chemical compositions of CNTs-HA coatings were characterized by various advanced methods. The scanning electron microscopy (SEM) images indicated that CNTs-HA coatings avoided the inhomogeneous dispersion of CNTs inside HA coating. The result show that the interfacial shear strength between CNTs-HA coating and the C/C composite matrix reaches to 12.86 ± 1.43 MPa. Potenitodynamic polarization and electrochemical impedance spectroscopy (EIS) studies show that the content of CNTs affects the corrosion resistance of CNTs-HA coating. Cell culturing and simulated body fluid test elicit the biocompatibility with living cells and bioactivity of CNTs-HA coatings, respectively.

1. Introduction

Crystallographically hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HA) is the dominant lattice structure of hard tissue [1] and it has been a material of major interest for load bearing implant application synthesized by different techniques [2–4]. The successful application of HA depends on its ability to induce bone regeneration and bone in growth at the tissue-implants interface without the intermediate fibrous tissue layer [5–7]. However, for the purpose of improving the long-term stability of HA coating, it is necessary to improve the cohesive strength of the HA coating and the bond strength between the HA coating and matrix. One of the most suitable solutions of this problem is to introduce reinforcement. Considering the biocompatibility of the composite coatings, carbon nanotubes (CNTs) have aroused great interests as reinforcements in composite materials because of their unique one-dimensional structure, high specific surface area and extraordinary intrinsic properties (mechanical and physical properties) [8–10]. Further, CNTs have the potential to strengthen and toughen HA without offsetting their bioactivities, and the biocompatibility of CNTs has been found to promote bone growth, to increase proliferation and to different osteoblast in-vitro [11,12]. These extraordinary properties of CNTs are expected to contribute to the improvement of poor cohesive strength of HA coating used as reinforcement in novel CNTs reinforced HA coating (CNTs-HA) [13–15].

At present, there are many techniques to fabricate CNTs-HA composite, such as plasma spraying, laser surface alloying, electrophoretic deposition, aerosol deposition, hot pressing sintering [8,16,17]. Studies on plasma spray formed CNTs-HA coating had been carried out by Kantest Balani [12,18], the results showed that the high temperature exposure in plasma spraying was suitable for preparing ceramic coatings on substrates with favorable adhesion strength. However, the high temperature caused the dissociation of HA powders to tricalcium phosphate ($Ca_3(PO_4)_2$, TCP). Chen et al. [19] had synthesized the HA-CNTs coating on Ti-6Al-4V by laser surface alloying. The high energy density laser beam caused the dissociation of HA powders to TCP and CaO. Moreover, the unfavorable reaction products (TiC) were formed due to the reaction between Ti alloy substrate and CNTs. Yu Bai et al. [20] synthesized CNTs-HA coating on titanium substrate by electrophoretic deposition. The biggest advantage of this method was the absence of high temperature exposure, without generating the dissociation of HA. But the major problem of this method was severe cracking, which limited the thickness and the strength of the coating to matrix. In addition, all these methods mixed the commercial CNTs with HA powers. Error caused by heterogeneous mechanical mixture couldn't be avoided, which might reduce the performance of CNTs as a reinforcement material.

In this work, high-purity CNTs were in-situ grown on the surfaces of carbon fiber reinforced carbon composites, or C/C composites for short,

* Corresponding authors.
E-mail addresses: jlliushoujie@126.com (S. Liu), lihejun@nwpu.edu.cn (H. Li), suyangyang@mail.nwpu.edu.cn (Y. Su), 1729299905@163.com (Q. Guo), zhangleilei@nwpu.edu.cn (L. Zhang).

http://dx.doi.org/10.1016/j.msec.2016.09.060
0928-4931/

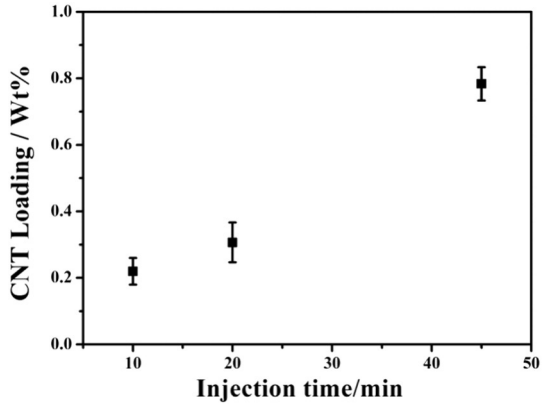

Fig. 1. Relationship between the CNTs loading on C/C composites surface.

using injection chemical vapor deposition (ICVD). CNTs grown on the C/C composite surface have the advantage over attaching CNTs in terms of the quantity, length, orientation and controllability size of CNTs that can be incorporated into the composites. Then we produced the CNTs-HA composite coatings by the pulsed electrodeposition. The aim of this study is to discuss the corrosion properties and in-vitro bioactivity of CNTs reinforced HA coating.

2. Experimental

2.1. Growing the CNTs onto C/C composites

C/C composites were prepared by chemical vapor infiltration (CVI) processing in Northwest Polytechnical University in China. C/C composites with a dimension of 8 mm × 8 mm × 2 mm were cut from the bulk C/C composites with a density of 1.78 g/cm^3. Then they were ultracleaned in turn by acetone, ethanol and distilled water, and dried at 60 °C. CNTs were grown onto C/C composites by using ICVD method at ambient pressure. sAt room temperature, the reactor was first purged with 300 sccm argon (Ar). After purging, the reactor was heated to 885 °C under Ar flow. At the growth temperature, the feeding solution of ferrocene (0.01 g/ml) in ethanol/ethylenediamine mixture (volume ratio of 4/1) was injected continuously into the reactor at a rate of 10 ml/h using a syringe pump. The injection time changed from 0 to 45 min, by which C/C composites doped with different contents CNTs were prepared. The weights of CNTs-C/C composites were measured by the electronic balance with a sensitivity of ±0.1 mg. Weight change percentage (ΔW%) of the samples was calculated by the following equation:

$$\Delta W\% = \frac{m_1 - m_0}{m_0} \times 100\%$$

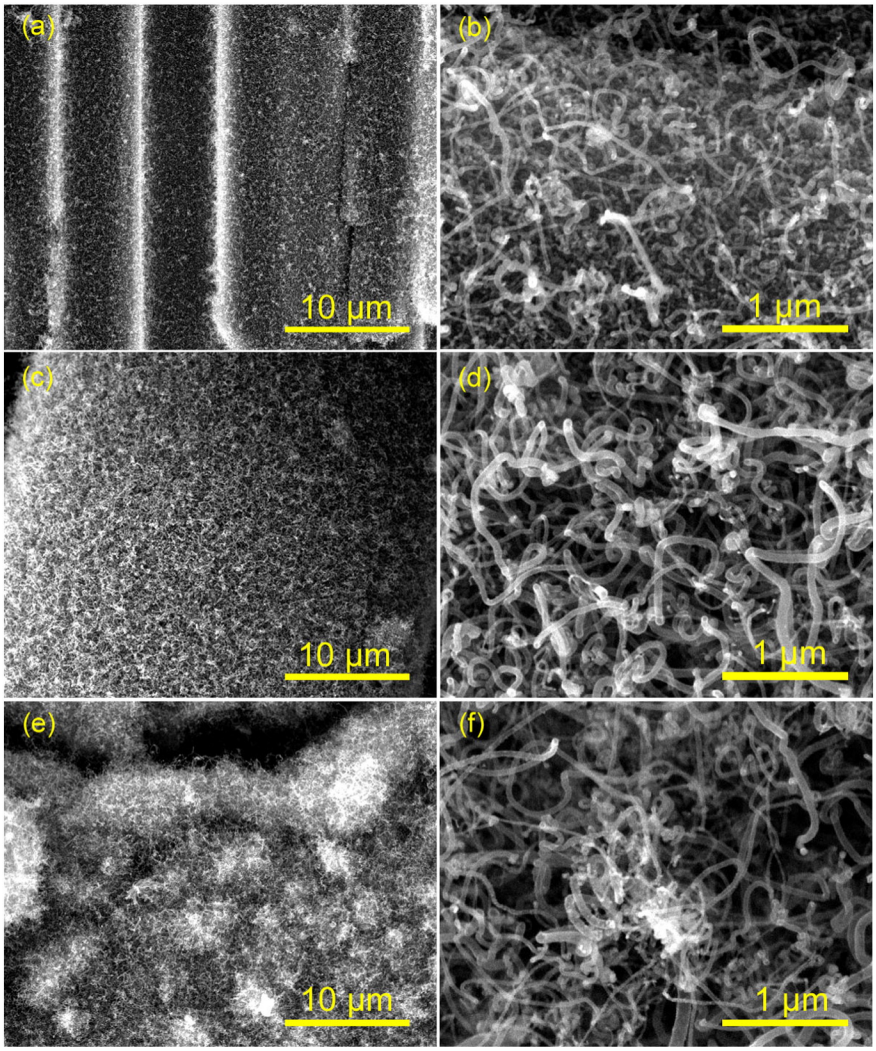

Fig. 2. SEM images of CNTs onto C/C composites with different injection time of CNTs: 10 min (a) and (b), 20 min (c) and (d), 45 min (e) and (f).