Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 36 (2010) 307–312
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Electrophoretic deposition of carbon nanotubes and bioactive glass particles for bioactive composite coatings

M. Charlotte Schausten [a], Decheng Meng [b], Rainer Telle [a], Aldo R. Boccaccini [b,*]

[a] Institute of Mineral Engineering (Institut für Gesteinshüttenkunde), RWTH Aachen, Mauerstraße 5, 52062 Aachen, Germany
[b] Department of Materials, Imperial College London, Prince Consort Road, London SW7 2BP, UK

Received 7 July 2009; received in revised form 18 July 2009; accepted 10 August 2009
Available online 23 September 2009

Abstract

The production of bioactive coatings consisting of 45S5 Bioglass® and mutli-walled carbon nanotubes (CNTs) by electrophoretic deposition (EPD) was investigated. In addition to pure Bioglass® coatings, the co-deposition and sequential deposition of Bioglass® particles (size <5 μm) and CNTs on stainless steel substrates were carried out in order to fabricate bioactive, nanostructured composite layers. The optimal experimental conditions were determined using well-dispersed suspensions by means of a trial-and-error approach by varying the relevant EPD parameters: applied voltage and deposition time. SEM images demonstrated the successful fabrication of Bioglass®/CNT composites by revealing their morphology and topography. The co-deposition of Bioglass® particles and CNTs resulted in homogenous and dense coatings exhibiting the presence of well-dispersed CNTs placed in-between micron-sized Bioglass® particles. This network of high-strength CNTs embedded in the glass layer could act as reinforcing element leading to higher mechanical stability of the coatings. The coatings obtained by sequential deposition offered a two-dimensional nanostructured fibrous mesh of CNTs covering the Bioglass® layer thus providing a controlled (ordered) nano-topographical surface. This surface nanostructure has the potential to promote the attachment and growth of osteoblast cells and to benefit the formation of bone-like nanosized hydroxyapaptite crystals in contact with body fluids.

Keywords: Electrophoretic deposition; Carbon nanotubes; Bioactive glass; Biomaterials

1. Introduction

The continuous application of implants and prostheses requires increased research efforts regarding optimization of their properties and functionality. The selection of materials and suitable production processes are decisive factors since they determine the biocompatibility and mechanical stability of the devices. A possibility to enhance the performance of metallic implants, in particular the bonding to bone tissue, is to coat them with bioactive layers [1–3]. The development of coatings based on bioactive inorganic materials (hydroxyapatite, bioactive glass) is the subject of numerous studies with the aim to improve tissue adhesion to the implant surface and therefore to induce better fixation of the device upon implantation [1–4].

Bioactive glasses are predestined materials for medical applications, in particular in orthopedic and dental implants, due to their excellent bioactivity and proved biocompatibility [5]. In contact with biological fluid, bioactive glasses form biologically active hydroxycarbonate apatite films structurally and chemically equivalent to the mineral phase in bone [5,6]. This feature permits strong interfacial bonding between implant and human tissue. However, contrarily to their outstanding bioactive potential, bioactive glasses exhibit low fracture toughness and limited mechanical strength in comparison with human bone. In case of excessive loading, the bioactive glass brittleness, even when used as coating on a metallic substrate, can lead to unacceptable loss of structural integrity and even failure of the devices. Furthermore coatings made of bioactive glass, which are subjected to heat treatments during processing, e.g. by viscous flow sintering, usually possess smooth surfaces which are not ideal for the attachment of cells, e.g. due to the lack of topographical features or optimized surface roughness [7]. In order to compensate these adverse effects a second

* Corresponding author. Fax: +44 207 594 6757.
E-mail address: a.boccaccini@imperial.ac.uk (A.R. Boccaccini).

0272-8842/$36.00
doi:10.1016/j.ceramint.2009.09.008

component can be used in combination with bioactive glass, effectively forming a composite material.

Carbon nanotubes (CNTs) attract enormous attention due to the extraordinary properties they exhibit which are determined by their unique structure and size [8]. The exploitation of these features in a variety of applications constitutes a wide and expanding research field [8,9]. The remarkable high mechanical strength and nanoscaled morphology of CNTs are the characteristics which make them interesting for biomedical applications, particularly for developing surfaces with nanoscaled and ordered fibrous structure [9–12]. For example, it has been shown that CNT layers provide an optimal nanomorphology for the adhesion of cells and their growth [13,14]. Combined with bioactive glasses, carbon nanotube coated surfaces also promote the formation of bone-like nanostructured hydroxyapatite crystals when the coatings are in contact with biological fluids [15]. Additionally, ultra-light but highly strong CNTs represent potential optimal reinforcing elements in bioactive glass matrices, as they can form a stiff network surrounding the glass particles.

The intrinsic complex processing capability of CNTs, due to their tendency to agglomerate which makes difficult their integration and dispersion into ceramic or glass matrices to form composites, is still a demanding challenge for technologists [16,17]. A very convenient technique for combination of CNTs and ceramic (nano)particles to form ordered arrays of CNTs and composite coatings is electrophoretic deposition (EPD) [12,15,18–20]. EPD relies on the presence of charged particles (or CNTs) in liquid suspensions which migrate and deposit onto an oppositely charged electrode upon application of an external electric field [21]. Electrophoretically deposited particles build layers of high microstructural homogeneity and packing density forming structurally robust deposits of varied thickness [21,22]. In addition to its simplicity, as electrophoretic deposition is a cost-effective method normally requiring simple equipment, EPD is also a versatile technique that can be used on a great variety of materials, i.e. ceramics, metals, polymers and glasses. Moreover the technique enables particulate materials of different size, shape and density to be co-deposited in order to generate uniform composite coatings of novel compositions [22]. Furthermore components of complex shape can be used as the working electrode, for example porous bodies such as scaffolds for tissue engineering or textile structures [15,22]. EPD is being increasingly considered as a convenient processing method for developing deposits and coatings from nanoparticles. In particular, CNTs become manageable by means of EPD since the method enables their manipulation in liquid suspension avoiding agglomeration problems, thus offering the possibility of their homogenous incorporation in composites [18–20].

The objective of the present research was to investigate the feasibility of using EPD to fabricate composite coatings of bioactive glass and (multi-walled) CNTs on stainless steel plates. The production of coatings by sequential deposition from single-phase suspensions was investigated as well as the co-deposition of both materials from diphasic suspensions. Whilst the bioactive glass layer represents the surface reactive component responsible for providing the physicochemical environment for bone attachment, the carbon nanotubes are intended to form a reinforcing network surrounding the glass particles. In addition, a sequentially deposited layer of pure CNTs on the Bioglass®/CNT coating should provide a topographical fibrous nanoscaled surface to enhance cell growth and proliferation.

2. Experimental

2.1. Materials

The bioactive glass powder used was 45S5 Bioglass® of composition (in wt.%): 45% SiO_2, 24.5% Na_2O, 24.5% CaO and 6% P_2O_5. The average particle size is approximately 5 μm, as determined previously [23]. The powder was used in as-received condition to produce suspensions containing 20, 25, 30 and 40 wt.% of Bioglass® particles in distilled water. The constituents were blended using a magnetic stirrer to support the dispersion process and to prevent sedimentation and agglomeration. All suspensions were treated ultrasonically afterwards for at least 20 min at ambient temperature in an ultrasonicator (Sonomatic, Langfor Ultrasonics) to achieve an adequate dispersion of the particles. The suspensions exhibited a pH value of ∼12.96 and it was observed that bioactive glass particles were negatively charged in these conditions in agreement with previous experiments [24].

Multi-walled carbon nanotubes (Nanocyl®-3100 series, Nanocyl, Belgium) were used. These CNTs are grown by catalytic carbon vapor deposition (CCVD) and subsequently purified to greater than 95% carbon. The as-received CNTs have an average length of about 1.5 μm. These were refluxed in 60 ml of mixed (1:3 volume ratio) concentrated nitric and sulphuric acid at 120° for 30 min. The oxidized tubes were then washed to pH 7. The aqueous CNT suspension had a concentration of 0.45 mg/ml. For the purpose of EPD, Triton X-100 and iodine 99.999% (Aldrich Chemical Company Inc., USA) were added in given concentrations to the CNTs dispersed in distilled water. Triton X-100 is used as an ionic surfactant due to its high dispersion efficiency while iodine is added to enhance the particle charging in the solution [15]. Table 1 displays the composition of the ingredients in suspension. CNTs in this type of suspension acquire a surface negative charge [15].

Diphasic suspensions were prepared by mixing equal parts of CNT and Bioglass® particle suspensions. The Bioglass® suspension contained 25 wt.% Bioglass® particles. The dispersion process was carried out using magnetic stirring and ultrsonication. Magnetic stirring was an essential step since the mixed suspensions had strong tendency to sedimentation

Table 1
Composition of the suspension used for EPD of CNTs.

	CNTs	Triton X-100	Iodine
Concentration per ml of distilled water [g/ml]	0.0006	0.0015	0.00005

and separation due to differences in density of the two ingredients. All measured pH values of the mixed suspensions were in the pH range 12.78–12.96.

2.2. Electrophoretic deposition

The electrophoretic deposition from three different kinds of suspensions on stainless steel plates was carried out. Firstly suspensions of only Bioglass® particles were used in order to optimize the EPD conditions in terms of voltage and time. The second series of experiments involved the EPD of mixed suspensions containing Bioglass® particles and multi-walled CNTs. Thirdly, the sequential electrophoretic deposition of Bioglass® particles and CNTs was conducted. Fig. 1 shows a schematic diagram of the EPD cell used. Since the used suspensions provided particles with negative surface charges (see above), the anode acted as substrate for the deposition.

The anode and cathode were made of 316L stainless steel plates (RS Components, Northants, UK) with dimensions of 10 mm × 30 mm × 0.2 mm. They were used as received except for a degreasing treatment in an ultrasonic bath with acetone. In order to neutralize the surface of the electrodes they were washed subsequently with distilled water followed by a final drying step with compressed air. After the cleaning process, the electrodes were connected to a DC power supply (Thurlby Thandar Instruments EL561, Cambridgeshire, UK). The EPD cell was additionally linked with a multimeter (Thurlby Thandar Instruments) to enable current intensity to be measured during the EPD process.

Electrophoretic deposition was carried out by setting a constant voltage in the range of 3–7 V, with deposition time ranging between 4 and 9 min and electrode separation of 1 cm. These conditions were determined by an optimization process based on a trial-and-error approach to generate deposits of satisfying thickness and uniformity which were visually inspected. All experiments were conducted at ambient temperature and samples were carefully and slowly pulled out of the suspension after EPD. Finally the samples were dried for at least 24 h at room temperature in normal air and in horizontal position to achieve coatings as homogeneous and smooth as possible.

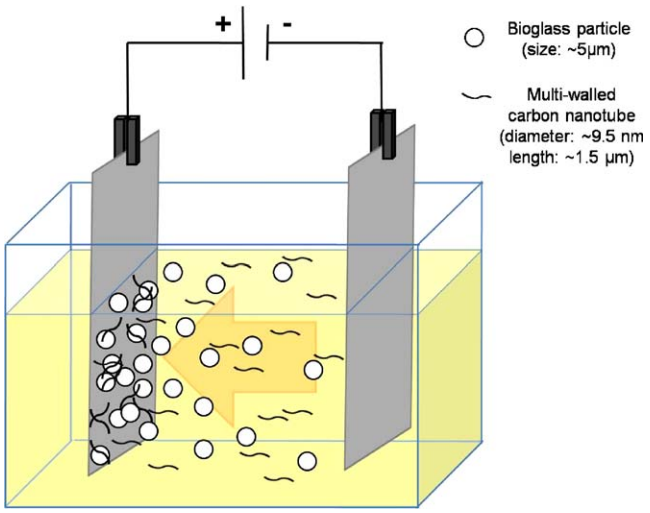

Fig. 1. Schematic diagram of the EPD cell during the co-deposition of CNTs and Bioglass® particles.

2.3. Characterization methods

Samples after EPD coating were firstly inspected visually to control their macroscopic quality and to change EPD conditions, if necessary. Scanning electronic microscopy (SEM) was carried out to examine the microstructure and morphological and textural features of the coatings. The pure Bioglass® samples were investigated using a JEOL 5610 SEM while the coatings containing carbon nanotubes were observed by means of field emission gun scanning electron microscopy (FEG-SEM) (LEO 1535).

3. Results and discussion

3.1. Bioglass® coatings

In the present experiments suspensions with different Bioglass® particle concentrations (20, 25 and 40 wt.%) were used. The results showed that the 25 wt.% suspension yielded the best coatings in terms of thickness homogeneity and

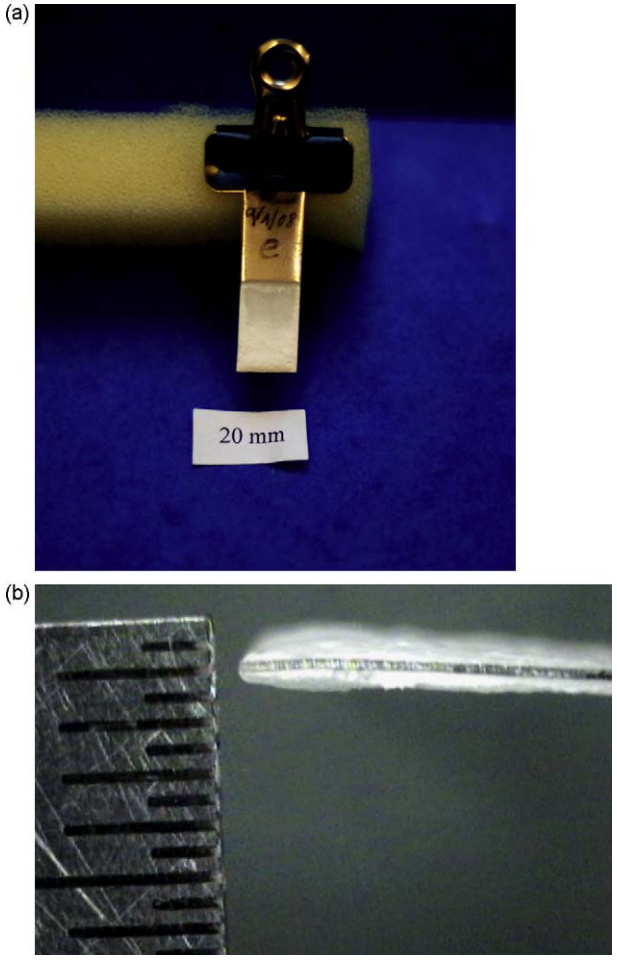

Fig. 2. Bioglass® coating obtained by EPD from a 25 wt.% suspension (5 V/7 min): (a) top view and (b) side view.

structural stability upon drying. Fig. 2a shows a typical Bioglass® coated sample made by EPD using 25 wt.% Bioglass® suspension at 5 V for 7 min. The side view of the sample in Fig. 2b shows the thickness of the coating on both sides of the stainless steel planar substrate. Coating of up to ~100 μm in thickness could be obtained.

Since substrates are placed vertically in the EPD cell, there is an influence of the gravitational force leading to particle sedimentation, which has an effect on the coating thickness uniformity. This sedimentation process was observed during EPD, which is reflected in the morphology of the resulting coatings. For example Fig. 2b shows the varying thickness of the coating near the lower end of the substrate. A possible way to alleviate this problem could be the use of horizontal electrodes, which is possible when using versatile EPD cells [25].

3.2. Composite Bioglass®/CNT coatings

As described above, the diphasic suspensions prepared for the electrophoretic co-deposition of CNTs and Bioglass® particles are composed of equal quantities of each single suspension. These contain 0.0006 g/ml CNTs and 25 wt.% Bioglass® particles. The tiny amount of carbon nanotubes in comparison to the Bioglass® fraction has a significant influence on the composition of the microstructure of the coating and its appearance. Deposition times between 5 and 6 min and voltages between 4 and 5 V were chosen for the electrophoretic co-deposition of the two materials. The SEM micrograph shown in Fig. 3 indicates that it is possible to achieve an extraordinary surface homogeneity of the composite coating.

The adhesion of the coating to the substrate was assessed only qualitatively in this investigation. It was observed that the coating did not crack or peel off from the substrate even if the substrate was bent, for example for preparing samples for SEM. This relatively high adhesive strength is a fundamental requisite for the prospective application of these coatings on biomedical implants. In addition, the nanostructured Bioglass®/CNT composite coating builds an ideal surface for the intended

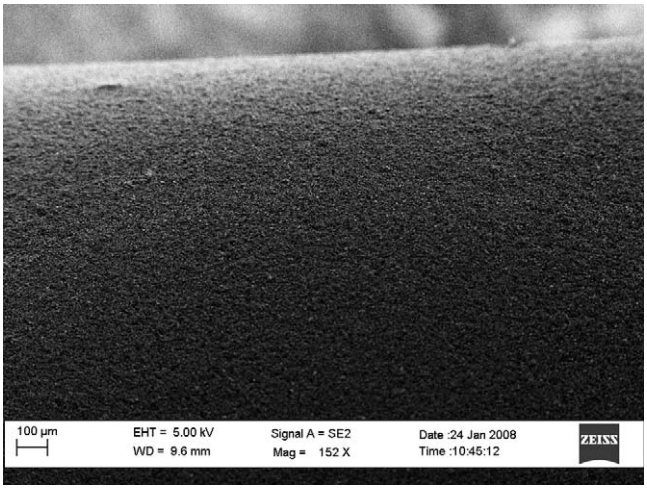

Fig. 3. SEM image of a composite Bioglass®/CNT coating (4 V/6 min) (top view) after drying, indicating high surface homogeneity and lack of large microcracks.

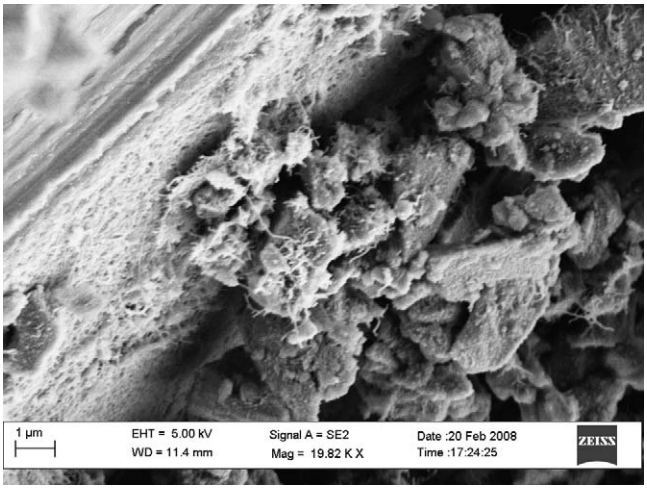

Fig. 4. SEM image of a composite Bioglass®/CNT coating obtained by EPD (4 V/6 min) (cross-section view).

improvement of bone tissue attachment. To observe the coatings cross sections, samples for SEM were prepared by sectioning through the coating manually using a razor blade. Fig. 4 is a SEM image of the coating cross-section. The coating thickness was measured to be ~30 μm. The micrograph reveals CNTs located in-between the individual Bioglass® particles and also placed directly on the surface of the substrate. This means that the CNTs are well dispersed in the coating layer and they could act as reinforcing element in the otherwise brittle Bioglass® coatings. A good dispersion of the carbon nanotubes is a prerequisite in order to build a rigid mesh or network of CNTs in the Bioglass® matrix. Clearly such CNT network must be maintained after sintering of the coating which will occur via Bioglass® viscous flow. The sintering behaviour of Bioglass® coatings obtained by EPD has been investigated elsewhere [24] but further research on the densification and microstructural evolution of Bioglass®/CNT composite coatings remains the focus of future work.

Higher voltage values gave rise to much thicker layers (of more than 100 μm). However this increased thickness was not constant and it was accompanied by strong irregularities in the coating structure. Visual inspection demonstrated that lower voltages caused thinner but more regular deposits whilst higher voltages increased the thickness but also the coating non-uniformity. By trial-and-error, it was found that most uniform and stable coatings were achieved using deposition voltages between 4 and 5 Volts and deposition time of 5–6 min. The SEM micrograph in Fig. 5 represents the typical fracture surface microstructure of a CNT/Bioglass® composite obtained at the optimal EPD conditions. The uniform woven layer of carbon nanotubes on the individual bioactive glass particles indicates that on deposition CNTs have preferentially deposited on the particles' surfaces. This result is important in terms of achieving high dispersion of the CNTs in the glass matrix upon sintering of the glass by viscous flow, as discussed elsewhere [26]. The high magnification image reveals a complete cover of the Bioglass® structure with randomly orientated carbon nanotubes. Furthermore the CNTs are seen to build connections between originally separated glass particles.

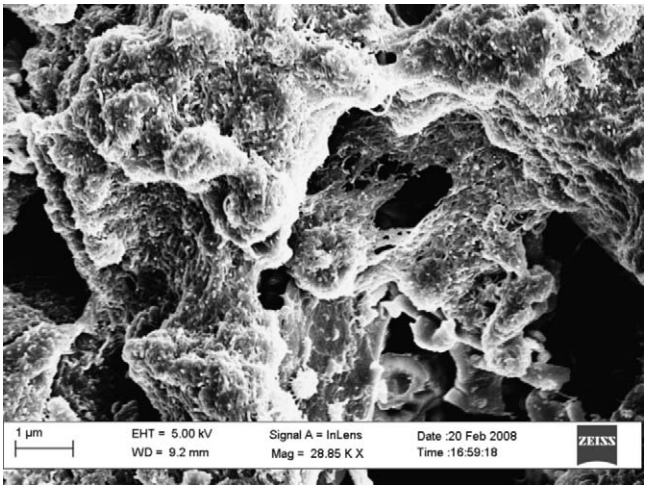

Fig. 5. SEM image of Bioglass®/CNT composite coating obtained by EPD (6 V/5 min). Fracture surface showing CNTs covering individual Bioglass® particles.

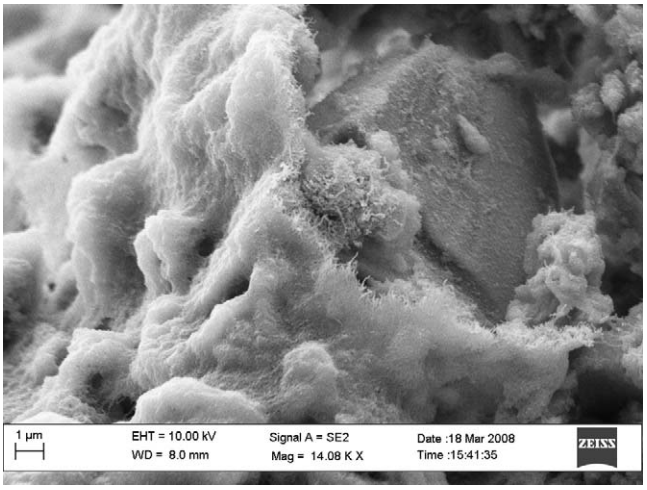

Fig. 6. SEM image of sequential Bioglass®/CNT coating by EPD, showing the cross-section of the coating characterized by a relatively uniform CNT coating on the previously deposited Bioglass® particles.

This behavior indicates the possible intended reinforcing function of CNTs in the Bioglass® matrix. It has been recently reported that CNTs can reduce the crack propagation in TiO_2/CNT films deposited by EPD [27] and mechanisms related to crack bridging and CNT pull-out are possible in these composite layers [28].

As discussed elsewhere [26], the poor mixing of CNTs and glass particles usually leads to lack of densification negating the reinforcing capability of CNTs in glass and ceramic matrices. This problem can be avoided in the present composites where EPD has produced a uniform distribution of CNTs on the surface of the individual Bioglass® particles. It is expected that upon sintering a uniform distribution of the CNT network in the glass matrix can be achieved as glass viscous flow will lead to closing the porosity (observed in Fig. 5).

3.3. Sequential (layered) Bioglass®/CNT coatings

The sequential electrophoretic deposition of Bioglass® particles and multi-walled carbon nanotubes was conducted in order to assess the effectiveness of EPD to produce an ordered fibrous nanotopography (provided by the CNTs) on the bioactive glass surface. The first Bioglass® coating was deposited as described in Section 3.1. Bioglass® coated substrates were then used as the deposition electrode (anode) for the subsequent CNT deposition. An electric field strength of 20 V and a deposition time of 4 min was used. Although small portions of the Bioglass® layer detached during EPD of CNTs, indicating that a heat treatment (pre-sintering) stage might be required, the remaining Bioglass® coating could be covered successfully with CNTs, as observed in the SEM image presented in Fig. 6.

The coating of carbon nanotubes is clearly observed (Fig. 6), exhibiting a high packing density of CNTs. A nanoscaled network was thus created by the random two-dimensional (planar) orientated CNT layer. The SEM image demonstrates the nanostructured roughness provided by the CNTs on the μm-sized bioactive glass particles. This feature is essential for the intended application of the CNT coated Bioglass®/CNT composite coatings in tissue engineering scaffolds and implants, considering the reported positive effect of nanofibrous topographies on osteoblast cell attachment and proliferation [29]. The sequential EPD method permits also a certain infiltration of the carbon nanotubes into the microscopic pores of the unsintered Bioglass® structure, as also shown in Fig. 6, where several CNTs are seen to be located on the micron-sized Bioglass® particles underneath the main CNT film. This partial infiltration could lead to a better adhesion between the CNT coating and the Bioglass® layer after sintering.

A comparison of the composite and multilayer Bioglass®/CNT coatings suggests that combination of both EPD methods will be required to produce coatings of optimal functionality. The composite Bioglass®/CNT coating obtained from diphasic suspensions should provide the required structural stability whilst a subsequent deposition of CNTs would lead to the desired fibrous nano-topographical surface to enhance cell attachment and proliferation. It should be pointed out also that, in the field of biomimetic materials for tissue engineering, Bioglass®/CNT coatings are of high interest as templates and scaffolds because they induce the rapid growth of biological hydroxyapatite nanosized crystals when the material is in contact with relevant biological fluids, e.g. simulated body fluid (SBF) [15]. The presence of CNTs should support the mineralization process of the surface leading to the formation of crystalline hydroxyapatite nanofibrous structures with CNTs acting as templates for biomineralisation, as discussed in the literature [30].

4. Conclusions

The production of bioactive coatings consisting of 45S5 Bioglass® and multi-walled carbon nanotubes using electrophoretic deposition method was presented. The EPD of Bioglass® particles yielded dense coatings with a thickness of up to ~100 μm. EPD parameters, such as concentration of the suspension, applied voltage and deposition time, were

found to influence the coating quality. Best results were achieved using suspensions with 25 wt.% Bioglass® particles deposited at 5 V for 7 min. SEM micrographs revealed the successful co-deposition of Bioglass® particles and carbon nanotubes forming composite layers of high relative density and uniformity. The quality of these deposits in terms of thickness and packing density was seen to be affected mainly by deposition voltage. The sequential EPD of Bioglass® particles and carbon nanotubes was carried out leading to a homogenous network of CNTs covering and partially infiltrating the Bioglass® layer. Besides investigating the sintering of the composite coatings, future work will involve the testing of the Bioglass®/CNT coatings in SBF in order to assess their ability to form biomimetic nano-hydroxyapatite crystals. Furthermore the general in vitro and in vivo biocompatibility of the Bioglass®/CNT coatings remains to be investigated, including issues related to possible toxicity effects of CNTs, in order to ensure their safe applications in the biomedical field.

Acknowledgement

The EU Erasmus Program is acknowledged for partial financial support for MCS for an internship at Imperial College London.

References

[1] J. Choi, D. Bogdanski, M. Koeller, S.A. Esenwein, D. Mueller, G. Muhr, M. Epple, Calcium phosphate coating of nickel–titanium shape-memory alloys. Coating procedure and adherence of leukocytes and platelets, Biomaterials 24 (2003) 3689–3696.

[2] A. Dey, A.K. Mukhopadhyay, S. Gangadharan, M.K. Sinha, D. Basu, N.R. Bandyopadhyay, Nanoindentation study of microplasma sprayed hydroxyapatite coating, Ceram. Int. 35 (2009) 2295–2304.

[3] A. Stoch, A. Brozek, G. Kmita, J. Stoch, W. Jastrzebski, A. Rakowska, Electrophoretic coating of hydroxyapatite on titanium implants, J. Mol. Struct. 596 (2001) 191–200.

[4] S. Sharma, V.P. Soni, J.R. Bellare, Chitosan reinforced apatite–wollastonite coating by electrophoretic deposition on titanium implants, J. Mater. Sci. Mater. Med. 20 (2009) 1427–1436.

[5] L.L. Hench, Bioceramics, J. Am. Ceram. Soc. 81 (1998) 1705–1728.

[6] G.A. Silva, O.P. Coutinho, P. Ducheyne, I.M. Shapiro, R.L. Reis, The effect of starch and starch-bioactive glass composite microparticles on the adhesion and expression of the osteoblastic phenotype of a bone cell line, Biomaterials 28 (2007) 326–334.

[7] A. Itala, H.O. Ylanen, J. Yrjans, T. Heino, T. Hentunen, M. Hupa, H.T. Aro, Characterization of microrough bioactive glass surface: surface reactions and osteoblast responses in vitro, J. Biomed. Mater. Res. 62 (2002) 404–411.

[8] M. Meyyappan, Carbon Nanotubes: Science and Applications, CRC Press, London, UK, 2004.

[9] B.S. Harrison, A.A. Attala, Carbon nanotube applications for tissue engineering, Biomaterials 28 (2007) 344–353.

[10] C. Kealley, M. Elcombe, A. Riessen, B. Ben-Nissan, Development of carbon nanotube-reinforced hydroxyapatite bioceramics, Physica B 385–386 (2006) 496–498.

[11] C. Lin, H. Han, F. Zhang, Electrophoretic deposition of HA/MWNTs composite coating for biomedical applications, J. Mater. Sci.: Mater. Med. 19 (2008) 2569–2574.

[12] C. Kaya, Electrophoretic deposition of carbon nanotube-reinforced hydroxyapatite bioactive layers on Ti–6Al–4V alloys for biomedical applications, Ceram. İnt. 34 (2008) 1843–1847.

[13] R.A. MacDonald, B.F. Laurenzi, G. Viswanathan, P.M. Ajayan, J.P. Stegemann, Collagen-carbon nanotube composite materials as scaffolds in tissue engineering, J. Biomed. Mater. Res. 74A (2005) 489–495.

[14] K. Balani, R. Anderson, T. Laha, M. Andara, J. Tercero, E. Crumpler, A. Agarwal, Plasma-sprayed carbon nanotube reinforced hydroxyapatite coatings and their interaction with human osteoblasts in vitro, Biomaterials 28 (2007) 618–624.

[15] A.R. Boccaccini, F. Chicatun, J. Cho, O. Bretcanu, J.A. Roether, S. Novak, Q. Chen, Carbon nanotube coatings on bioglass-based tissue engineering Scaffolds, Adv. Funct. Mater. 17 (2007) 2815–2822.

[16] R. Andrews, D. Jacques, D. Qian, T. Rantell, Multiwall carbon nanotubes: synthesis and application, Acc. Chem. Res. 35 (2002) 1008–1017.

[17] S.-K. Kim, H. Lee, Fabrication of patterned single-walled carbon nanotube film using electrophoretic deposition, Ultramicroscopy 108 (2008) 1005–1008.

[18] A.R. Boccaccini, J. Cho, J.A. Roether, B.J.C. Thomas, E.J. Minay, M.S.P. Shaffer, Electrophoretic deposition of carbon nanotubes, Carbon 44 (2006) 3149–3160.

[19] I. Singh, C. Kaya, M.S.P. Shaffer, B.C. Thomas, A.R. Boccaccini, Bioactive ceramic coatings containing carbon nanotubes on metallic substrates by electrophoretic deposition, J. Mater. Sci. 41 (2006) 8144–8151.

[20] W. Sheng-Chang, H. Bo-Chin, Field emission properties of Ag/SiO_2/carbon nanotube films by pulsed voltage co-electrophoretic deposition, Thin Solid Films 517 (2008) 1245–1250.

[21] P. Sarkar, P.S. Nicholson, Electrophoretic deposition (EPD): mechanisms, kinetics, and application to ceramics, J. Am. Ceram. Soc. 79 (1996) 1987–2002.

[22] A.R. Boccaccini, I. Zhitomirsky, Application of electrophoretic and electrolytic deposition techniques in ceramics processing, Curr. Opin. Solid State Mater. Sci. 6 (2002) 251–260.

[23] J.A. Roether, A.R. Boccaccini, L.L. Hench, V. Maquet, S. Gautier, R. Jerome, Development and in-vitro characterisation of novel bioresorbable and bioactive composite materials based on polylactide foams and Bioglass® for tissue engineering applications, Biomaterials 23 (2002) 3871–3878.

[24] D. Krause, B.C. Thomas, C. Leinenbach, D. Eifler, E.J. Minay, A.R. Boccaccini, The electrophoretic deposition of Bioglass® particles on stainless steel and Nitinol substrates, Surf. Coat. Technol. 200 (2006) 4835–4845.

[25] E. Stoll, P. Mahr, H.-G. Krüger, H. Kern, B.J.C. Thomas, A.R. Boccaccini, Fabrication technologies for oxide–oxide ceramic matrix composites based on electrophoretic deposition, J. Eur. Ceram. Soc. 26 (2006) 1567–1576.

[26] A.R. Boccaccini, D.R. Acevedo, G. Brusatin, P. Colombo, Borosilicate glass matrix composites containing multi-wall carbon nanotubes, J. Eur. Ceram. Soc. 25 (2005) 1515–1523.

[27] W. Jarernboon, S. Pimanpang, S. Maensiri, E. Swatsitang, V. Amornkitbamrung, Effects of multiwall carbon nanotubes in reducing microcrack formation on electrophoretically deposited TiO_2 film, J. Alloys Compd. 476 (2009) 840–846.

[28] J. Cho, A.R. Boccaccini, M.S.P. Shaffer, Ceramic matrix composites containing carbon nanotubes, J. Mater. Sci. 44 (2009) 1934–1951.

[29] K.L. Elias, R.L. Price, T.J. Webster, Enhanced functions of osteoblasts on nanometer diameter carbon fibers, Biomaterials 23 (2002) 3279–3287.

[30] S. Aryal, S.R. Bhattari, R. Bahadur, M.S. Khil, D.R. Lee, H.Y. Kim, Carbon nanotubes assisted biomimetic synthesis of hydroxyapatite from simulated body fluid, Mater. Sci. Eng. A 426 (2006) 202–207.