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# Accelerated biomimetic apatite with functionality graded materials of hydroxyapatite/YSZ by electrophoretic deposition

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## Abstract

The aim of this work is to improve the bioactivity of hydroxyapatite/yttria stabilized zirconia by using functionally graded materials (FGMs) on 316L stainless steel as a substrate using electrophoretic deposition technique. Four layers of functionally graded materials (100% HA, 70%HA +30%YSZ +30%HA +70%YSZ, 100% YSZ) were deposited on thin layer of chitosan deposited on substrate. 0.5 g/L chitosan was used as a binder between particles layers of FGM. Solvent which used to prepare FGM layers consist of alcohol and distilled water (ethanol, 5vol.% water and containing 0.5 g/L of chitosan dissolved in 1 vol.% acetic acid) with 3g/L for each HA and YSZ. The pH value was performed and fitted at 4. Single and FGM layers were tested in vitro using simulated body fluid (SBF) with two periods (two and four weeks) in order to evaluate the bioactivity of coatings. The results demonstrated the good buildup of apatite which was increased with increasing the thickness of FGM layer. New phase of HA with high intensity were appeared as obtained from XRD. The layers have a good adherent with the substrate after immersing in SBF.

## Introduction

There is a high request for materials that have a good mechanical and biomedical properties which used for implants in biomedical applications. One of important bioactive material for dental and orthopedic application is hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) because of it was in similar with chemical composition of the natural apatite and it has biocompatibility with hard tissues and also with muscle and skin tissues. It was bonded directly to the bones without cytotoxic effects. But HA was limited in major load bearing applications because it has poor mechanical properties as compared to bone.

To enhance its mechanical properties, it was used with other bioceramic materials. yttria-stabilized zirconia was considered to be an advantageous inert ceramic biomaterial with biomedical applications. Y-TZP has fulfilled the biomechanical requirements that used in orthopedic and its application in this field has been therefore intensively studied. This material bas high strength, high toughness at room temperature, high compressive strength, high modulus, very good biocompatibility and the good compromise they represent between fracture resistance, therefore it was used in orthopaedic prostheses as a replacement for metallic material.

Bioceramic materials (bioactive and bioinert materials) are used for coating metal substrate such as 316Lstainless steel, because this metal has been utilized for a long time for implants applications because of their excellent corrosion and mechanical resistant properties. But 316L stainless steel exhibit pitting corrosion and crevice that causes cell toxicity by releasing Cr and Ni ions in human body. Functionally graded materials (FGM) could be used to combine different materials with different properties. Electrophoretic deposition (EPD) was one of surface engineering methods, it enabled the co- deposition of various ceramic or/and polymeric materials that produced dense, high homogeneity and tailored thickness. It has many advantages like: purity, high uniformity for coating, possibility of using complex shaped substrates, short deposition time of coatings and easy control of the coating thickness.

The aim of this work is to evaluate the bioactivity of functionally graded (FGM) HA-YSZ produced by EPD and showed how FGM accelerated the nucleation of HA.

## Methods and Materials

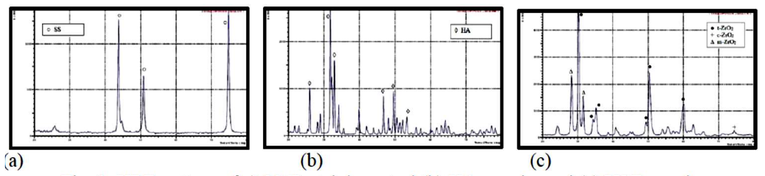
316L stainless steel as a substrate and three types of powders were used in current work. nanohydroxyapatite (reagent grade, powder, synthetic), chitosan (medium molecular weight with a degree of deacetylation of about 85%) (Purchased from Sigma Aldrich) and yttria stabilized zirconia ($ZrO_2$- 3mol $Y_2O_3$). Sand blast samples have been used with dimensions (2cm, 1cm, 2mm) to deposit coating layers. 0.5g/L of chitosan was dissolved in 1% acetic acid and then mixture of (94% ethanol + 5% deionized water) was added to prepare the solution of chitosan thin layer which deposited on 316L stainless steel. In order to obtain the best dispersion, the solution was stirred for 24 hours. 3g/L of HA and YSZ concentration with 0.5g/L of chitosan that dissolved in 1% acetic acid 94% ethanol + 5% deionized water are used for Functionally graded materials which consist of four layers deposited on chitosan layer a 100% HA, 70% HA + 30% YSZ, 30% HA +70% YSZ and 0% HA + 100% YSZ). The solutions of FGM are stirred for 5 hours to obtain the best homogeneity. pH value for all solutions was performed at 4. The distance between the two electrode (anode and cathode) was 10 mm and EPD was performed at (50V, 5 min and 30ºC) for hydroxyapatite and (30V, 6 min and 30ºC) for YSZ.

Simulated body fluid five times concentrated (SBF ×5) was prepared and pH value for this fluid was adjusted at 7.4 using HCl or NaOH as required. Two groups from coated samples (with area 2 cm2) were immersed in the prepared (SBF ×5) solution for 14 and 28 days. The solution SBF was changed every 7 days, after immersing the samples, thermally treated at 100C in tubular furnace for 1 hr. The samples tested by XRD, optical microscopy used to evaluate the formation of hydroxyapatite (HA) on the coatings and to evaluate results.

## Results and Discussions

Bioactivity of the coatings was an important key aspect to ensure subsequent bone/implant integration *in-vivo* conditions, therefore coatings of the single (100% HA) and FGM layers (100%HA and FGM) were tested by immersion in SBF for two and four weeks to evaluate their bioactivity. 316L stainless steel, two types of powders (HA an YSZ) coating layers of single and FGM layers before and after immersion in SBF for two periods (two and four weeks) were characterized by XRD analyzed. Optical microscopy was used to investigate morphology of coatings layers.

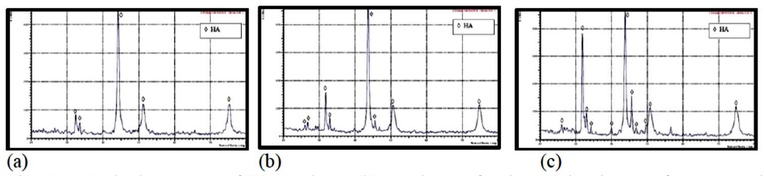
Phases of stainless steel before coating are showed in Fig. 1 a, it was observed three different 2θ peaks are related for austenitic 316L stainless steel [74.76° (220), 50.84° (200) and 43.76° (111)]. They identified according to JCPDS card No 33-0397., nano-HA, ytrria stabilized zirconia powder. Fig. 1 b shows the peaks corresponding to the phase of hydroxyapatite (211), (300), (222), (213) and (321) according to JCPDS card No 09-0432. Wider peaks profile might detect the low crystallinity and/or small crystal size of the nanoparticles. Fig. 1 c. shows the different phases for yttria stabilized zirconia with different diffraction peaks. It was observed that the dominant phase is tetragonal like (111), (311), (220), (202) and (200). with monoclinic phase ( $\bar{1}11$) and (111) according to JCPDS cards Nos. 27-0997, 37-1484 and 42-1154 respectively.




(a) (b) (c)

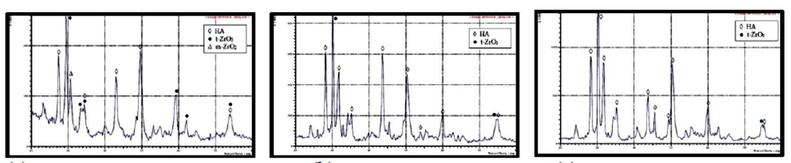
Fig. 1. XRD pattern of a) 316L stainless steel (b) HA powder and (c) YSZ powder

XRD for single layers of HA deposited on substrate shows the presence of different diffraction peaks as compared with powder of HA. This can be attributed to the chitosan particles which act as a binder material and as a coating thin layer on 316L stainless steel substrate which affected the XRD peaks. Fig. 2 a shows the phases of HA layer (400), (112), (410) and (324). The highest intensity for HA was found at 2θ 44.25°. after immersion in SBF, it was observed for sample of single layer of HA the existence phases of HA (113) at peak 43.5°. The phases (211) and (113) appeared strongly at 31.7°and 43.7°with high intensity as compared with sample before immersion as shown in Figs. 2 b and 2 c.




(a) (b) (c)

Fig. 2. XRD is the pattern of (a) HA layer (b) HA layer after immersion in SBF for two weeks (c) HA layer after immersion in SBF for four weeks

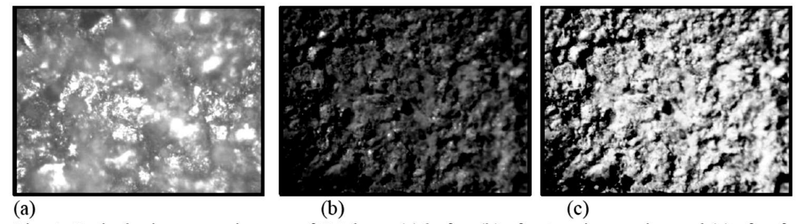



(a) (b) (c)

Fig. 3. XRD pattern of (a) FGM layers (b) FGM layers after two weeks immersion in SBF (c) FGM layers after four weeks immersion in SBF

For functionally graded composite coatings the diffraction peaks combined two materials. Fig. 3 a shows phases FGM such as (101), (002) (211) and (202). They reveal the presence of tetragonal phases. The monoclinic phase was appeared at (111). HA phases were also appeared such as (102), (113) and (213). After immersion in the solution, the phases of HA are revealed strongly as shown in Figs. 3 b and 3 c. Many peaks of HA (113), (102), (213) and (420) appeared on the sample of FGM after immersion in SBF for two weeks as shown in Fig. 4 b. The peaks of (211) appeared with higher intensity with the same sample after four weeks immersion. In addition, many new HA phase appeared at peaks at (211), (321), (301) and (420) as shown in Fig. 3 c

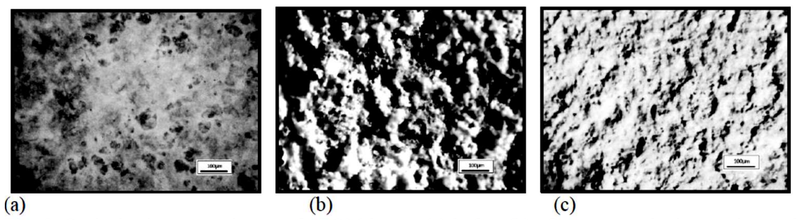
Fig. 4 showed the images of optical microscopy for coating layer coating for 100% HA before and after immersion in SBF. It was noticed that the coating was thick, rich and homogenous layers of apatite formed on the surface of all samples and there is no uncoated area. After soaking for two weeks the surface of the substrate was fully covered with smaller and larger apatite particles with more agglomeration as observed. Increasing the immersion interval to four weeks, the surface becomes thicker and denser due to the increasing of apatite nucleation. This is an indication to the formation of the apatite layer on the surface of the mineralized bio ceramic materials



(a) (b) (c)

Fig. 4. Optical microscopy images of HA layer (a) befor, (b) after two immersion and (c) after four weeks imerssion

The optical images for functionally graded layers before and after immersion are shown in Fig. 5. It had been observed that thick, dense apatite layer was formed after immersion. This layer had fully covered the coating after four weeks of immersion, this is corresponding to the best build up to HA coating layers on FGM layer.



(a) (b) (c)

Fig. 5. Optical microscopy images forFGM layers (a) befor, (b) after two weeks immersion and (c) after four weeks imerssion

## Conclusions

1-The hydroxyapatite revealed on the surface of all samples after two weeks of interaction with SBF. It appeared more strongly after four weeks.

2-There are various thickness and crystenallity of the layers from hydroxyapatite nucleation obtained as confirmed by XRD.

3-The FGM layers are denser and thicker than single layer which indicated best nucleation for HA and better bioactivity with good adhesion layers

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