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 1vol% 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.

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, 3.5mol Y, 2). 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 produce 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 was used for Functionally graded materials which consists of four layers deposited on chitosan layer 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 for all solutions was performed at 4. The distance between the two electrodes (anode and cathode) was 10 mm and EPD was performed at 50V, 5 min and 30°C for hydroxyapatite and (30V, 6 min and 30°C) 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 100°C 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 20 peaks are related for austenitic 316L stainless steel [74.76° (220), 50.84° (200) and 43.76° (111)]. They identified according to ICPSD card No 33-0397, nano-HA, yttria-stabilized zirconia powder. Fig. 1 b shows the peaks corresponding to the phase of hydroxyapatite (211), (300), (222), (213) and (321) according to ICPSD 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 (111) and (111) according to ICPSD cards Nos. 27-8997, 37-1484 and 42-1154 respectively.

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), (212), (213) and (422) 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), (201) and (422) 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 homogeneous 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.

Conclusion
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 crystallinity of the layers from hydroxyapatite nucleation were determined by the immersion eases confirmed by XRD and EDX.
3-The FGM layers are denser and thicker than single layer which indicated best nucleation for HA and better bioactivity with good adherence layers.

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References