Picosecond Laser based Additive Manufacturing of Hydroxyapatite Coatings on Cobalt Chromium Surfaces

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Abstract
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Keywords
Hydroxyapatite, Cobalt Chromium, Ball-Milling, Picosecond Laser Treatment, Scanning Electron Microscope

Disciplines
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Comments

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1. Introduction

Picosecond laser based additive manufacturing process was used to coat the cobalt chromium (CoCr) plates with the nanophase hydroxyapatite powder [1]. Hydroxyapatite (HA) with the formula Ca\textsubscript{5}(PO\textsubscript{4})\textsubscript{3}(OH) is a mineral form of calcium, that is found in the teeth and bones of the living creatures. Therefore, it is commonly used in the medical purposes as a scaffold to replace amputated bones or as a coating to allow bone ingrowth into prosthetic implants [2].

Hydroxyapatite coatings on medical implants are conventionally formed using plasma spray process [3]. The plasma sprayed implants have demonstrated
better bone ingrowth and osseointegration than conventional implants [3, 4]. However, the plasma sprayed coatings may suffer from decomposition due to high processing temperatures. In addition it is difficult to control the porosity and surface roughness of the coating [3].

Mixtures of HA and polymeric binder materials have been utilized to generate porous three dimensional scaffolds that are bioactive and promote osseointegration [5]. Hence, porous coatings with desired three dimensional surface characteristics and roughness may promote better bonding and osseointegration of biomedical implants [4].

Nanoscale HA has generated great interest in the research community due to several advantages over the micron sized HA including better bioactivity and biocompatibility. The nanoscale HA possesses very high surface area and surface roughness, which leads to better cell adhesion and cell-matrix interaction. The ultrafine structure of nanoscale HA is very similar to the mineral found in hard tissues and thus has very good biocompatibility. It also exhibits greater resorbability and bioactivity compared to micron sized HA. Additionally, nanoscale HA has demonstrated enhanced densification and sinterability. Thus mitigating problems associated with high temperature sintering such as micro crack formation [6].

The additive manufacturing of nanophase HA coating on cobalt-chromium surfaces was performed using a high repetition picosecond pulsed laser. Sol-gel processes are used to synthesize nanophase HA. Synthesized powders were suspended in volatile organic solvents to prepare nanoscale HA inks for coating. Picosecond laser irradiation of inks was utilized to coat nanoscale HA on cobalt chromium surfaces. A layer by layer coating process was used to obtain HA coating along the laser irradiated pattern. Scanning electron microscopy was used characterize the surface roughness and chemical composition of obtained coatings.

2. Materials and Experimental Methods

2.1. Nanoscale Hydroxyapatite ink preparation:

Hydroxyapatite (HA) nanoparticles were synthesized by the sol-gel technique. The chemicals used for this synthesis were calcium nitrate tetrahydrate Ca(NO₃)₂·₄H₂O, phosphorus pentoxide (P₂O₅) and ethyl alcohol (C₂H₅OH). The chemicals were purchased from Sigma Aldrich having a purity greater than 98%.

For the preparation of HA, 0.02 M Ca(NO₃)₂·₄H₂O was dissolved in 15 mL of C₂H₅OH. Similarly, 0.006 M P₂O₅ was dissolved separately in 15 mL of C₂H₅OH. The P₂O₅ was dissolved slowly and in a controlled manner to C₂H₅OH, avoiding excess temperature change since this is an exothermic reaction. After complete dissolution, the phosphorus precursor solution was added drop wise to the calcium precursor solution with continuous stirring. The final solution was then stirred for 5 h at room temperature, which led to gelation and aging. The gel was then air dried in an oven at 80 °C for 24 h. The dried gel was heat treated at 600 °C for 1 h [1, 7-8]. Fig. 1 shows the schematic representation of the synthesis process.

![Fig. 1. Schematic representation of the HA synthesis process.](image_url)

The synthesized powders were ball milled with steel and tungsten carbide balls for one hour to obtain uniform particle distribution and break down the large aggregates. The ball milled powders were suspended in acetone and methanol at mass ratio of 1:6 and sonicated to obtain two different inks for additive manufacturing.
2.2. Picosecond laser System

Picosecond laser with an average power of 3 W, a pulse width of 110 ps, and a wavelength of 1064 nm was used for the deposition process. The laser system is equipped with a galvano mirror stage to enable irradiation of samples along a programmed pattern.

2.3. Coating Procedure

A layer by layer printing process was used to coat hydroxyapatite on the cobalt chromium surface along a grid like pattern of 3 mm X 3 mm composed of intersecting horizontal and vertical lines spaced about 60 µm as shown in Fig 2. The cobalt chromium surfaces were cleaned with acetone, methanol and distilled water.

A pipette was used to deposit 2 µl solution of the HA ink on the surface. Due to hydrophilic nature of the CoCr surface, deposited ink droplet completely covered the area of the desired pattern. Picosecond laser with 1064 nm wavelength, repetition rate of 50 KHz, average power setting of 3 W and average linear speed of 3.3 mm/s was used to irradiate the ink covered surface along the grid pattern.

The procedure was repeated was repeated for two different inks – HA powder suspended in methanol and HA powder suspended in acetone.

2.4. Coating Characterization

X-ray diffraction employing a Siemens D500 instrument (Siemens, New York) was utilized to determine the particle size and crystalline orientations of the as-synthesized HA powders. The as-synthesized powder, ball-milled powders, AM inks and coated surfaces were imaged using SEM (FEI Quanta-250 SEM instrument) at 10 kV accelerating voltage. The HA nanoparticle samples were coated with thin layer of Iridium before SEM imaging. SEM images were used to determine the particle size and distribution as well as the coating morphology. Energy dispersive Spectroscopy to determine the chemical composition of the coated surfaces.

3. Results

Composition and structural information of the HA nanoparticles were studied using X-ray diffraction with Cu Kα radiation (λ = 1.5406 Å). The diffractometer was operated at 45 kV and 30 mA over the 2θ range of 20–60° at a scan rate of 0.02 °/s. The XRD pattern of the as-synthesized HA nanoparticles is shown in Fig. 2. It was observed that the Bragg angles and peak intensities matched well with the reference JCPDS file [7, 9, 10]. The crystal structure of HA nanocrystals was hexagonal P6₃/m [10]. The presence of CaO crystalline phase was not detected. This indicates that the sample was entirely composed of HA nanoparticles [10].

Fig. 2. Coating pattern used for HA deposit on CoCr surfaces

The morphology of the synthesized HA nanoparticles was studied using the scanning electron microscope. Fig. 3 shows the SEM image of as-
synthesized HA nanoparticles. Due to the drying and annealing process, there is considerable amount of agglomeration in the as-synthesized powders. However, there are some regions that show the HA nanoparticles of size ~600 nm. The annealing process has caused the nanoparticles to agglomerate and fuse together to form short chain like structures [9, 11].

SEM image of the powders after ball milling procedure is shown in Figure 4 and shows agglomerations of uniform particles that are approximately 75 nm in diameters. Ball milling was able to break down the fused chain like structures into nanometer scale powders. The uniform sized particles could be suspended in methanol and acetone using sonication to produce stable suspensions for the laser-assisted additive printing.

![Fig. 4. SEM image of HA nanoparticles](image1)

![Fig. 5. SEM image of HA nanoparticles after ball-milling process (50000x magnification)](image2)

SEM images of the HA coatings on CoCr implants obtained from irradiating the surface along a grid pattern in presence of methanol and acetone suspensions area shown in Figure 6 and Figure 7, respectively. The layer-by-layer coating process was repeated 10 times to obtain a thickness of around 40 µm.

In both cases, the printed surfaces were cleaned using soft brushes and sonication to remove the unbound suspension before the SEM imaging. The images show that the HA coating is strongly adhered to the surface only along the irradiated pattern. The high magnification view of HA coating obtained from the methanol suspension in Figure 6 (B) shows that HA particles have fused together to cover the surface with strongly adherent coating with fractal like roughness texture. The coating texture shows large few micron sized domes decorated with smaller submicron sized asperities. The smallest asperities on the coated surface are larger than the 75 nm sized particles obtained after the ball-milling procedures.

![Fig. 6. SEM images of the HA coatings obtained on CoCr surface from irradiating methanol suspension of ball-milled HA particles. A) Low magnification image showing that coating is adherent only to the laser irradiated paths; B) High magnification image of the coating indicating the micrometer scale fractal roughness.](image3)
Figure 7 shows that coatings obtained from acetone suspensions are also adhered only along the path irradiated by the picosecond laser. However the higher magnification image of the acetone suspension based coating shown in Figure 7(B) shows clear differences in the micron scale coating textures in comparison to methanol suspension derived coatings. The acetone based coating shows smooth globular zones interspersed with smaller asperity covered domes. The smoother globular zones may be the result of laser induced fusion of the HA particles during laser irradiation. The rough asperity covered areas have asperities that are the same size as the ball milled particles. The size of the asperity indicates that the rough areas are created due to embedding of individual particles into the underlying matrix of the fused particles.

The EDS spectrum obtained on both the coated surfaces are shown in Fig 8 (A) and (B), for methanol and acetone based suspension, respectively. The spectrum show that elemental composition of the surface is dominated with Phosphorus, Calcium, Cobalt, Chromium and Oxygen elements. The relative magnitude of the Phosphorus and Calcium are higher on the samples coated using acetone based suspension. These result indicate that acetone based suspension is more efficient in coating the Co-Cr surface.

4. Discussion

Picosecond laser based additive manufacturing process was utilized to coat CoCr surfaces with HA coating that hierarchical surface roughness. Coating process utilized 75 nm sized HA particle suspension produced using ball milling of synthesized product.
is strong enough to withstand sonication. We are currently characterizing the strength of the particle-particle and coating/surface adhesion.

The coating deposited from acetone suspension provide more surface coverage than the ones that were deposited using methanol suspensions. The reason for this may be due to volatility difference between the two organic fluids. The short pulse width of the picosecond laser may also have different interactions with acetone and methanol suspensions.

The surface profile of the HA coatings on dental and orthopedic implants determines the adsorption of proteins, osteoblastic cells and thus the rate of osseointegration [4]. It is hard to obtain biomimetic nanoscale surface roughness and nanophase crystal structure in conventional processes such as plasma spray coating. Hence there has been interest in non-conventional process that can coat implant surfaces with desired roughness and crystal structure.

The current approach of combining of sol-gel synthesis, ball milling and low-power high repetition rate picosecond laser based additive manufacturing is able to achieve desired nanoscale surface roughness, nanoscale crystallinity and microscale surface patterning. The fractal nature of surface roughness at nanoscale will be useful for protein absorption and thus may be used to produce drug eluting implant surfaces. In addition, the low power irradiation may ensure that nanophase crystal structure of HA is maintained during the coating. Preserving the nanophase crystal structure of HA will promote resorption of the coating and thus result in faster osseointegration with implants. In addition, the laser path during the coating process may be designed to produce desired microscale surface patterns of grooves and holes that promote contact guidance of osteoblastic cells and thus minimize the scar tissue development during osseointegration. Further work is continuing to characterize the coating adhesion strength and bioactivity of the coated HA surfaces.

5. Conclusions

Nanoscale rough coatings of nanophase HA on CoCr surfaces were deposited using laser based additive manufacturing process. The manufacturing approach is based on sol-gel synthesis, ball milling and low-power high repetition rate picosecond laser based additive manufacturing is able to achieve desired hierarchical surface roughness, nanoscale crystallinity and microscale surface patterning. The results show that low power lasers with picosecond pulse width may be used to fuse the ball-milled HA to obtain a nanoscale fractal rough coating. Nanoscale rough biomimetic coating may enhance the biocompatibility and bioactivity of implant surfaces.

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References


