Nano-Hydroxyapatite Coated Acetabular Cup Implant by Electrophoretic Deposition

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ABSTRACT

A nanostructural hydroxyapatite (HA) coating was deposited to the porous Ti6Al4V acetabular cup implants using a room temperature electrophoretic deposition (EPD) process in order to achieve the improved bonding strength between the implants and cells, fast healing, good corrosion resistance and long-term stability after implantation. The micropores created in the coating will improve the bioactivity and healing processes. In order to let the acetabular cup implant with complicated profile achieve homogeneous HA coating along the high island and low valley regions, a compensation electrode was designed and prepared. The combined EPD with a dip coating processes was able to compensate for the coating profile and led to a homogenous coating on both valley and island areas. The microstructure of the coating was characterized using microscopy. The corrosion property was tested by using electrochemical method.

Using this developed coating process can make uniform HA coatings on very complicated implant surfaces. Comparing to the coating made by plasma thermal spray, the EPD HA coating can cover internal pores, and exhibits a better adhesion to the substrate which achieves stronger shear and bond strengths. In addition, electrochemical corrosion test demonstrates that the EPD HA coating possesses a significant improved corrosion resistance compared to the coating prepared using plasma thermal spray HA coating. The success of EPD HA coating to cup implant with porous surface established a basis for enhancing the application of HA coating in orthopedics.

Key words: nano-hydroxyapatite, electrophoretic deposition, acetabular cup implant, porous coating, bond strength, corrosion resistance.

1. INTRODUCTION

Coating hydroxyapatite (HA) films onto the surfaces of Ti alloy acetabular cup porous implants will be able to increase the bioactivity, improve the blood coagulation and accelerate the patient's healing process after implantation. However, a commercial plasma thermal sprayed HA coating experiences dissolution and cracking of the HA coating in human body fluid due to the formation of amorphous hydroxyapatite phase originating from the rapid quenching of thermal spray, as well as the inability to coat the porous holes and inner surfaces of complicated geometry due to the inherent line-of-sight process of thermal spray.

A room-temperature electrophoretic deposition (EPD) process, followed by scheduled low temperature sintering, has been applied to deposit HA coatings on porous titanium alloy implants since 1990 [1]. The EPD possesses the unique feature of being suitable for porous surfaces and complex shaped implants while maintaining a controllable grain size. However, sintering shrinkage cracking and Ti/HA interfacial reaction prohibited this process from further development and commercialization. HA coatings have been successfully deposited on porous Ti plates using this process. However, after a low-temperature calcination HA (200-900 ^{o}C), it was found that severe cracking of the HA after sintering occurred because of thermal expansion mismatch [2-3].

A novel approach by using a nanostructured HA coating on titanium implants through the EPD process to improve the performance of the Ti implants has been conducted [4-7]. A nano HA coating with a grain size of ~50 nm and micrometer sized porosities can provide higher surface bioactivity and blood coagulation than conventional micrometer sized HA coatings without micropores on the surface leading to a significantly faster early-stage bone healing process. The EPD can uniformly coat HA nanoparticles into the pores of Ti beaded implants, while the conventional thermal spray process cannot do. In our previous studies, we have found that the EPD process is capable of making coatings possessing unique HA nanograins combined with microporous surface structures while using non-porous Ti6Al4V substrates [7]. Our previous research findings included significant improvements in coating to substrate bond strength (3 times) and corrosion resistance (300 times) [4-7]. The consequent development is logically applying these findings to approach real orthphotics and dental products.

In this study, we utilize the EPD process to coat nano-HA composite to porous titanium acetabular cup implants. The formed n-HA coating with a nanograin size and micrometer sized porosities provides higher surface bioactivity and blood coagulation when compared to conventional micrometer sized HA coatings without surface micropores leading to a significantly faster early-stage bone healing process. The developed HA nanocoating should possess good corrosion resistance, which will be identified. Efforts will also be put on optimizing HA/medical glass composite and concentration to achieve the best bioactivity, and avoid the HA coating crack. In addition, the engineering processing issues and various problems to fabricate uniform HA nanocoatings on porous acetabular cup implants will be investigated and addressed in this project.

2. EXPERIMENTAL AND RESULTS

Implant substrate. Semi-sphere Ti6Al4V alloy cup with a diameter of Ø65.5 mm was used for the coating substrate. The surface of the acetabular cup implant has a porous surface layer as shown in figure 1.

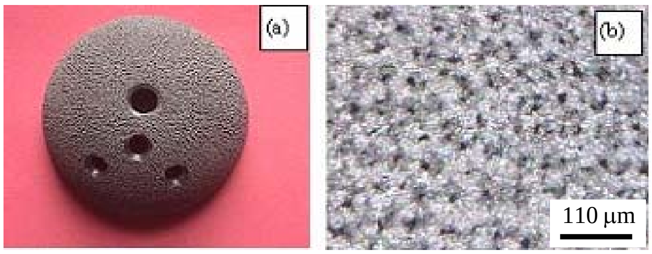

Fig. 1. Acetabular cup implant with porous surface (a) with low magnification and (b) high magnification

Slurry. HA-glass slurry was prepared by ball milling HA-medical glass powders with the binder PVB for 24 hours. The concentration of the powder in the slurry was adjusted to an optimal result of 8 wt%.

EPD electrode and fixture. The EPD electrode and cup holder mixture were designed as shown in figure 2 and fabricated using bulk graphite. In order to keep a uniform distribution of the electric field along the cup implant semi-sphere surface, the profile of the electrode design keeps a similar distance between the electrode and cup implant surface.

Fig. 2. Electrode (lower part) and cup implant holder fixture (upper part) for the porous hip substrate.

An EPD unit was custom designed and fabricated. The inner semi-sphere 3-dimensional toroidal was made in order to keep a uniform distribution of the electric field. A rotation function was designed to control the drying process and quality of the as-fabricated coatings. This EPD unit has a slurry delivery system that protects the evaporation of carrier solvent. The slurry was stored in a sealed tank. During deposition, the slurry was pumped into the chamber of the EPD unit, and continuously circulated.

Deposition. EPD process was carried out using a graphite electrode and implant fixture as shown in figure 2 with rotational capabilities. A voltage of 20 volts and deposition time of 3 minutes was used for the EPD processing. In order to avoid cracking and achieve a uniform HA coating, spinning of the as-coated samples with a rate between 100 to 500 rpm was conducted. 2-5 cycles of deposition were performed.

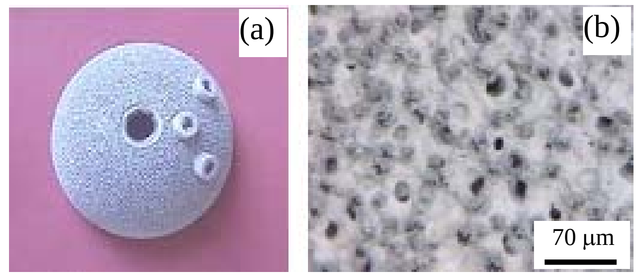

Fig. 3. HA coated acetabular cup implant with porous surface (a) with low magnification and (b) high

Experiments indicate that the coating quality is associated with the slurry density and fixture rotation speed. The porous surface of the implant was found to deposit much faster than the smooth surface using the same concentration of slurry. Hence, in order to avoid cracks in the coating, a thinner HA-glass slurry is desired. Secondary, the coating quality is sensitive to the fixture rotation speed. A stripe pattern would form if the rotation were either too fast, or too slow. It was found a rotation rate of 200 rpm could lead to a uniform HA coating. Using a HA-glass slurry with 8 wt% powder, with a rotation speed of ~200 rpm, a good quality HA-glass coating was obtained as shown in figure 3.

Sintering. The sintering of the HA-glass nanocomposite coating includes the removal of the PVB binder at 600°C in air, and a sintering processing at 950°C under a stream of nitrogen. As shown in figure 4, the sintered HA-glass coating exhibits a unifrom, crack-free, and continuously densified coating of excellent quality.

Fig. 4 Sintered HA/glass coated cup implant

Dip coating. The HA-glass slurry was prepared as described in EPD slurry except for a small adjustment to the amount of glass used. The sintered EPD HA-glass coated implants were immersed in the HA-glass slurry for 30-60 seconds, and then rotated as described in the previous section. The dip coating needs to be performed for 3-5 cycles.

Due to uneven distribution of the electric field, the EPD will lead to a thicker coating in the peak area, and a thinner layer in the valley area. Dip coating can compensate for the shortages of the EPD. In addition, after sintering, the HA-glass coating becomes electrically insulating; therefore the EPD process will not be able to be used for further coating, while dip coating is without limitation. Due to the rough surface of the sintered implant, only 3 pass of dip coating can lead to a continuous HA-glass coating without any cracks as shown in figure 5.

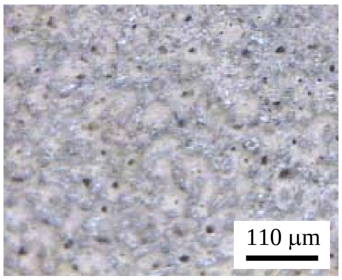

Fig. 5. HA/glass dip coated acetabular cup implant

The second sintering. The 2nd sintering was carried out after the drying of the HA-glass dip coating. The sintering is exactly the same as the first sintering. Figure 6(a) exhibits the images for the 2nd sintered HA-glass implant for 5 cycles. This sintered implant shows a homogenous HA-glass deposition layer without cracking. The sintered HA-glass coating exhibits good quality.

Etching. The glass in the HA/glass composite usually exhibits poor bioactivity. In order to remove the glass on the top of the composite coating, the sintered cup implant was etched within diluted HF acid. The etched implants were cleaned in DI water using an ultrasonic bath. Through HF etching, glass will be partially removed, and the remained HA with complicated profile and large specific surface area will increase its bioactivity. The visible white layer of the surface is the evidence for the etching effect – after partially removal of the glass, the white HA coating becomes visible as shown in figure 6(b)

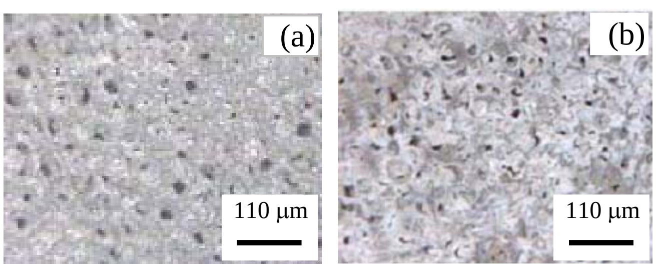

Fig. 6 (a) 2nd sintered and (b) etched n-HA coated acetabular cup implants

Corrosion resistance. The electrochemical corrosion tests were conducted at an analytical electrochemical system. Experimentally, the HA coated implants is acted as the working electrode, platinum as the counter electrode, and calomel as the reference electrode. The Hank solution diluted 10 times was selected and as the bath solution. Using a Potentiostat/Galvanostat, Model 173, the scanning range was from –0.3 to 3.0 V with a scan rate of 0.01mV/second. For comparison, plasma thermal sprayed HA coated implants were selected. The test of the EPD coated implant was performed under the same condition.

The test results are shown in figure 7. The corrosion resistance for the EPD HA coated implant is as 8 folds as the plasma thermal sprayed implants. Given the thin EPD HA coated layer, the actual improvement of corrosion resistance over for the thermal sprayed EPD HA coated implants would be much higher if the same thickness of the coating was compared.

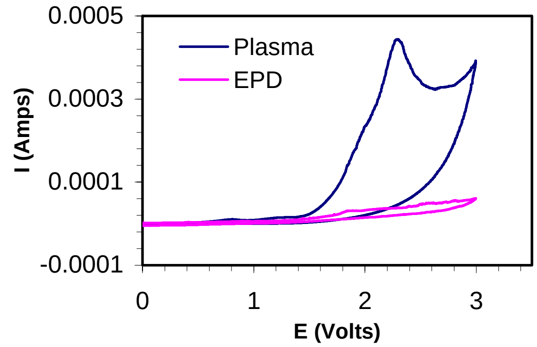

Fig. 7. Electrical polarized corrosion curves of EPD HA nanocoating and thermal sprayed micrometer sized HA coating on Ti6Al4V implants

3. CONCLUSIONS

1) An acetabular cup implant EPD electrode was designed and fabricated using bulk graphite. An acetabular cup implant EPD deposition unit and controllable rotating fixture was designed and fabricated. This system with multi-parameter control functions enables a good quality coating to be produced.

2) The effect of many factors; including slurry concentration and fixture rotation speed on the HA-glass coating quality, have been tested and identified. An optimized EPD and dip coating processing was achieved by using appropriate fixture rotation (~200 rpm) assistance. In this case, a homogeneous HA-glass coating can be obtained.

3) Using the previously optimized sintering process, a good densified HA coating without cracks and defects can be achieved.

4) The EPD nano HA coated implants offers 8 folds better corrosion resistance than plasma thermal sprayed HA coated implants.

ACKNOWLEDGEMENTS

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