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Induction plasma sprayed nano hydroxyapatite coatings on titanium for orthopaedic and dental implants

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ABSTRACT

This paper reports preparation of a highly crystalline nano hydroxyapatite (HA) coating on commercially pure titanium (Cp-Ti) using inductively coupled radio frequency (RF) plasma spray and their *in vitro* and *in vivo* biological response. HA coatings were prepared on Ti using normal and supersonic plasma nozzles at different plate powers and working distances. X-ray diffraction (XRD) and Fourier transformed infrared spectroscopic (FTIR) analysis show that the normal plasma nozzle lead to increased phase decomposition, high amorphous calcium phosphate (ACP) phase formation, and severe dehydroxylation of HA. In contrast, coatings prepared using supersonic nozzle retained the crystallinity and phase purity of HA due to relatively short exposure time of HA particles in the plasma. In addition, these coatings exhibited a microstructure that varied from porous and glassy structure at the coating-substrate interface to dense HA at the top surface. The microstructural analysis showed that the coating was made of multigrain HA particles of ~200 nm in size, which consisted of recrystallized HA grains in the size range of 15–20 nm. Apart from the type of nozzle, working distance was also found to have a strong influence on the HA phase decomposition, while plate power had little influence. Depending on the plasma processing conditions, a coating thickness between 300 and 400 μm was achieved where the adhesive bond strengths were found to be between 4.8 and 24 MPa. The cytotoxicity of HA coatings was examined by culturing human fetal osteoblast cells (hFOB) on coated surfaces. *In vivo* studies, using the cortical defect model in rat femur, evaluated the histological response of the HA coatings prepared with supersonic nozzle. After 2 weeks of implantation, osteoid formation was evident on the HA coated implant surface, which could indicate early implant-tissue integration *in vivo*.

1. Introduction

Long-term fixation of metallic implants in bony tissues is still a concern for load bearing implants. Because of poor osteoconductivity, metallic implants often get encapsulated by fibrous tissue, which prolong the healing time. To address these limitations, HA coating was developed as a surface modification technique to improve osteoconductivity of metallic implants. A variety of coating techniques have been used to coat metallic implants with HA [1,2]. Among them, plasma spraying is the most widely used commercial technique due to its ease of operation, high deposition rate, low substrate temperature, and low cost. A relatively low substrate temperature during the coating process is especially advantageous, as the mechanical properties of the implant materials are not compromised due to plasma spraying. Radio frequency (RF) and direct current (DC) are the two main types of plasma used for HA coating [3–5]. Axial feeding of precursor sol/solution/particle, which reduces turbulence in the plasma, is an important advantage of RF induction plasma spray process [4]. The induction plasma spray is an electrode free system, which eliminates the risk of contamination from the electrodes and is advantageous especially for preparing high purity HA coatings.

Problems associated with conventional plasma sprayed HA coatings include decomposition of HA, amorphous calcium phosphate (ACP) formation, and cracking. Plasma sprayed HA coating typically contains tricalcium phosphates (TCP in α/β form), oxyhydroxyapatite (OHA), tetracalcium phosphate (TTCP), and calcium oxide (CaO) with different dissolution properties [1,6–8]. Phases such as TTCP or CaO do not have any proven bioactivity and also dissolve faster than other calcium phosphate phases. Although partial dissolution of HA coating is necessary for intimate biological bonding, excessive dissolution can lead to an unstable implant–bone interface, which not only affect the bioactive fixation but also lead to coating disintegration [9]. Therefore, TTCP and CaO phases have to be minimized in the coating to improve bioactivity, stability, and implant life. ACP dissolves faster than its crystalline form and thus, adversely affects the bioactive fixation process [10,11]. Although post deposition heat treatment can improve coatings crystallinity, the volume changes associated with amorphous to crystalline phase transformation can generate large stresses, leading to coating disintegration or delamination [12]. Moreover, during the post deposition heat treatment, the microcracks that are created during

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plasma spraying merge to form larger cracks that can result in mechanical degradation of HA coating [12]. Post deposition heat treatment might also degrade mechanical properties of metallic substrate.

The objective of present work is to create plasma sprayed HA coating with minimum phase decomposition and high crystallinity without compromising the adhesive bond strength. Previous studies on plasma sprayed HA coating generally reported the coating properties in terms of crystallinity [6–8], phase decomposition [13], dissolution properties [14] and mechanical properties [9]. Effects of precursor powder and substrate on coating properties have also been reported [15,16]. This study investigates the role of different plasma nozzle design on coating properties of HA in terms of phase decomposition and ACP phase formation. A 30 kW inductively coupled RF plasma system equipped with either normal or a supersonic nozzle was used for HA coating preparation. Coatings were characterized for phase purity and crystallinity using X-ray diffraction and FTIR. To ensure adequate mechanical integrity, adhesive bond strength of the coatings was measured. *In vitro* bone cell–materials interactions were evaluated on the plasma sprayed HA coatings, prepared with supersonic nozzle, to understand the cytocompatibility. *In vivo*, performances of the similarly prepared HA coatings were assessed using an intramedullary defect model in rat femur.

2. Experimental procedure

2.1. Coating preparation

Commercial grade 150 μm sized HA powder (Monsanto, USA) of was used to coat 2 mm thick commercially pure Ti substrate (Grade 2, President Titanium, MA, USA) of 99.7% purity. Prior to coating, Ti substrates were sandblasted, washed ultrasonically in deionized water, and then cleaned with acetone to remove any organic materials.

A 30-kW inductively coupled RF plasma spray system (Tekna Plasma Systems, Canada), equipped with an axial powder feeding system, was used for the HA coating preparation. Argon (Ar) was used to create the plasma. The gas flow rate was expressed as standard liters per minute (slpm). In this study, coatings were initially prepared at 25 kW and at 110 mm working distance using normal and supersonic plasma nozzles to understand the effect of nozzle design on coating properties. From now onwards, the HA coatings prepared with normal and supersonic nozzles will be called as NHA and SHA, respectively. Schematic diagram of these two nozzles are shown in Fig. 1. At first, both NHA and SHA coatings were prepared and compared, and later on all of the coatings were prepared with only supersonic nozzle, as the SHA coatings showed better properties in terms of coating crystallinity and phase purity. To study the effects of plate power and working distances on coating properties, SHA coatings were prepared with three levels of plate power and working distances. Table 1 lists the plasma spray parameters used for SHA.

2.2. Coating microstructure, phase, and chemical analysis

Coated samples were mounted, sectioned, and polished for microstructural observation. Polished sections were then etched with a solution of hydrofluoric acid (49% by acidometry), nitric acid (15.8 N) and distilled water in a ratio of 1:2:25 to reveal coating microstructure. Microstructural characterization of the coatings was performed using a field emission scanning electron microscope (FEI 200 F, FEI Inc., OR, USA).

Siemens D500 Krystalloflex X-ray diffractometer using Cu Kα radiation at 35 kV and 30 mA at room temperature was used to determine different phases in the coating with a Ni filter over the 2θ range between 20° and 60°, at a step size of 0.02° and a count time of 0.5 s per step. To identify the chemical groups present in the coating and its crystallinity, the coating was scraped off from the substrate and grounded for FTIR analysis. ATR-IR (attenuated total reflection-infrared) spectra were recorded on a FTIR spectrometer (FTIR, Nicolet 6700, ThermoFisher, Madison, WI). Samples were placed on an ATR diamond crystal and spectra were obtained in the wave number ranging from 400 to 4000 cm^{-1}.

2.3. Mechanical properties

The bond strength of the as sprayed HA coatings was evaluated using a standard tensile adhesion test (ASTM C633) set up, where five replicates were used. The counter Ti substrate was also sand blasted and attached to the surface of the HA coating using epoxy resin as an adhesive glue. After curing in an oven at 120 °C for 2 h, the fixtures were subjected to a tensile test at a constant cross head speed of 0.0013 cm/s until failure. The adhesive bond strength was calculated as: failure load/ sample area. The data were reported as mean ± standard deviation.

2.4. In vitro cell culture

All samples were sterilized by autoclaving at 121 °C for 20 min. Established human osteoblast cell line hFOB 1.19 (ATCC, Manassas, VA, USA) was used. Cells were seeded onto the samples placed in 24-well

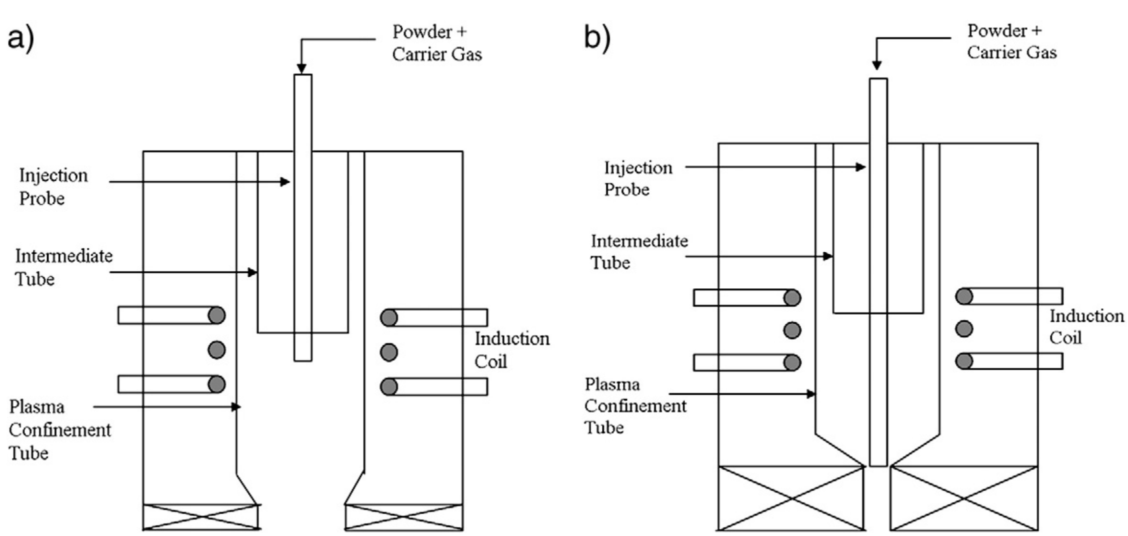

Fig. 1. Schematic of (a) normal and (b) supersonic plasma nozzle.