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Compositionally graded hydroxyapatite/tricalcium phosphate coating on Ti by laser and induction plasma

Mangal Roy *, Vamsi Krishna Balla, Amit Bandyopadhyay, Susmita Bose

W.M. Keck Biomedical Materials Research Laboratory, School of Mechanical and Materials Engineering, Washington State University, Pullman, WA 99164, USA

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ABSTRACT

In this study we report the fabrication of compositionally graded hydroxyapatite (HA) coatings on Ti by combining laser engineering net shaping (LENS™) and radio frequency induction plasma spraying processes. Initially, HA powder was embedded in the Ti substrates using LENS™, forming a Ti–HA composite layer. Later, RF induction plasma spraying was used to deposit HA on these Ti substrates with a Ti–HA composite layer on top. Phase analysis by X-ray diffraction indicated phase transformation of HA to β-tricalcium phosphate in the laser processed coating. Laser processed coatings showed the formation of a metallurgically sound and diffused substrate–coating interface, which significantly increased the coating hardness to 922 ± 183 Hv from that of the base metal hardness of 189 ± 22 Hv. In the laser processed multilayer coating a compositionally graded nature was successfully achieved, however, with severe cracking and a consequent decrease in the flexural strength of the coating. To obtain a structurally stable coating with a composition gradient across the coating thickness a phase pure HA layer was sprayed on top of the laser processed single layer coatings using induction plasma spray. The plasma sprayed HA coatings were strongly adherent to the LENS™–TCP coatings, with adhesive bond strength of 21 MPa. In vitro biocompatibility of these coatings, using human fetal osteoblast cells, showed a clear improvement in cellular activity from uncoated Ti compared with LENS™–TCP coated Ti and reached a maximum in the plasma sprayed HA coating.

1. Introduction

Hydroxyapatite (HA) and tricalcium phosphate (TCP), owing to their chemical similarity to natural bone, have been widely used in bone graft substitutes [1–4]. However, the inherent brittleness of HA and TCP has limited their uses to non-load bearing applications, such as coatings on metal implants, bone fillers, bone cements, posterior spinal fusions and craniomaxillofacial surgery [5,6]. HA, due to its chemical stability among all of the calcium phosphates under physiological condition, is used as a coating on metallic implants to improve osteoconductivity and bone–tissue integration, while TCP finds applications in temporary bone graft substitutes, where slowly resorbed TCP encourages bone–tissue in-growth and bone remodeling [6–9].

A number of different coating techniques have been employed for the preparation of HA-coated metallic implants, which includes solution-based techniques [10,11], thermal spraying [12,13] and laser-based techniques [9,14–16]. Some excellent reviews of these coating processes have also been written [12,17,18]. Although the surface chemistry determines the initial biological response, the long-term stability of a coated implant is primarily dictated by its in vivo physical and mechanical stability. A dense and strongly adherent coating will certainly minimize spalling and can reduce osteolysis, generally triggered by loosened implant particles. Laser assisted processes have been widely studied to produce a mechanically stable calcium phosphate coating on Ti [9,16,19]. Among these processes, pulsed laser deposition (PLD) [12], laser irradiation [16] and laser cladding [15,19] have been investigated. Although PLD has been successfully used to prepare strongly adhering HA coatings, the process is limited to thin coatings (<5 μm), which makes it questionable for long-term in vivo stability [12]. Comparatively, laser cladding can produce thick ceramic coatings on metallic substrates with a composition gradient across the coating thickness [9], which can significantly enhance interfacial strength.

We have already demonstrated that laser engineered net shaping (LENS™) can be used to prepare tricalcium phosphate (TCP) coatings, composed of a Ti–TCP composite, with thicknesses ranging from 200 to 400 μm [9]. It has been shown that the volume fraction of TCP in the coating and its hardness can be tailored by changing the processing parameters, such as laser power, laser scan speed and powder feed rate. To take full advantage of the bioactivity of calcium phosphate coatings the coating surface should contain 100% calcium phosphate, instead of a Ti–calcium

* Corresponding author. Tel.: +1 5093393746.
E-mail address: mangal_roy@mail.wsu.edu (M. Roy).

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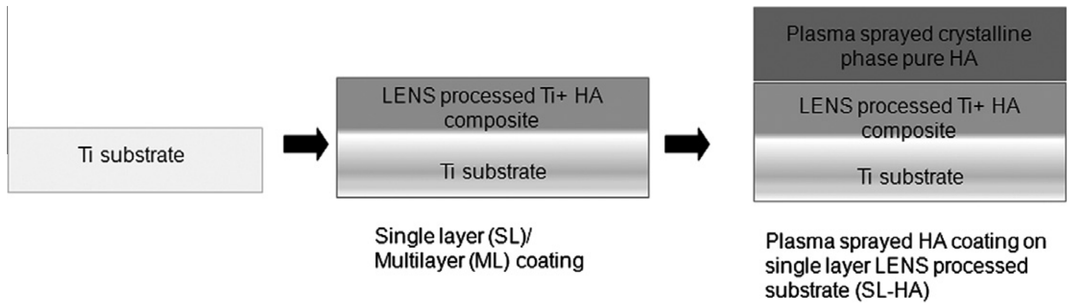

Fig. 1. Graded coating scheme.

phosphate composite layer. Plasma spraying is the most popular process for the preparation of HA coatings on biomedical devices due to certain advantages, like simplicity, high deposition rates, low substrate temperature and economic viability [20]. However, plasma sprayed calcium phosphate-based ceramic coatings suffer from low crystallinity, poor interfacial bonding and a sharp coating–substrate interface [21,22]. In addition, a high cooling rate can introduce cracks in the coatings, which can reduce the adhesion strength between the substrate and the coated ceramic. Therefore, to enhance the long-term stability of HA/TCP-coated Ti implants the coating should be highly crystalline and strongly bonded to the substrate with a diffused interface.

In this paper we report the fabrication of compositionally graded HA coatings on Ti by combining LENS™ and radio frequency (RF) induction plasma spraying processes. The coating scheme is represented in Fig. 1. Initially, HA powder was embedded in the Ti substrates using LENS™, forming a Ti–HA composite layer. Later, RF induction plasma spraying was used to deposit HA on these Ti substrates, with a Ti–HA composite layer on top. The advantage of such a combination is obvious: the laser processed Ti–HA composite layer acts as a diffuse and strong interface between the substrate and the plasma sprayed HA coating, forming a compositionally graded coating, which can eliminate problems associated with sharp interfaces and also enhance the crystallinity of the HA phase in the coatings due to lower cooling rates. The present work focuses on processing; coating characterization and in vitro biocompatibility of the compositionally graded HA coatings on Ti prepared using both LENS™ and plasma spraying.

2. Experimental procedures

2.1. Coating preparation

Commercial grade HA powder having a particle size ranging from 45 to 150 μm was used to coat a 2 mm thick commercially pure Ti substrate (Grade 2, President Titanium, MA) of 99.7% purity. The Ti substrate was cleaned with acetone to remove organic material from the surface prior to coating. A LENS™ 750 (Optomec, Albuquerque, NM) unit with a 0.5 kW continuous wave Nd:YAG laser was used to create a Ti–HA composite layer on the Ti substrate. To reduce the oxidation of Ti, the coatings were fabricated in a glove box containing a controlled atmosphere with a total O_2 content of less than 10 ppm. Coatings were made at a laser power of 500 W, a scan speed of 15 mm s^{-1} and a powder feed rate of 13 g min^{-1}. These parameters were selected based on previously published work to process good quality coatings [9]. In the present work single layer deposition resulting in Ti–HA composite layers and multilayer depositions (surface scanned 3 times) resulting in a 100% HA layer on to of the Ti–HA composite layer were carried out. Multilayer depositions were aimed at evaluating the feasibility of direct laser fabrication of 100% HA coatings on the Ti substrate.

Ti–HA composite coatings prepared using LENS™ was further deposited with a top layer of 100% HA using RF induction plasma spraying. Commercial grade 150 μm size HA powder was used for plasma spraying. A 30 kW inductively coupled RF plasma spray system (Tekna Plasma Systems, Canada), equipped with an axial powder feeding system, and was used for the coating preparation. Argon gas was used for plasma generation. In this study coatings were prepared at 25 kW and at a 110 mm working distance using a supersonic plasma nozzle. These parameters were selected based on prior optimization of the process for good quality coatings. In the supersonic plasma nozzle the HA particles were introduced in the lower region of the plasma torch with a velocity of 510 m s^{-1}, much higher than that of conventionally used plasma nozzles. The shorter distance traveled at higher speed makes the residence time for HA particles very short, at 290 μs almost 15 times shorter than conventional plasma spraying. Table 1 lists the plasma spray parameters used in the present work. Hereafter single layer (SL), multilayer (ML) and plasma sprayed (SL-HA) coatings will be referred to by their acronyms (Fig. 1).

2.2. Microstructure and phase 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 at a ratio of 1:2:25 to reveal the coating microstructure. Microstructural characterization of the coatings was performed using a field emission scanning electron microscope (FEI 200F, FEI Inc., OR). A Siemens D500 Krystalloflex X-ray diffractometer using CuK_α radiation at 35 kV and 30 mA at room temperature was used to determine the constituent phases in the coatings with a Ni filter over the 2θ range 20–60°, at a step size of 0.02° and a count time of 0.5 s per step.

2.3. Mechanical properties

The bond strength of the LENS™ processed and graded 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

Table 1
Experimental conditions.

Central gas flow rate (s.l.p.m.)	25 Ar
Sheath gas flow rate (s.l.p.m.)	60 Ar + 6 H_2
Carrier gas flow rate (s.l.p.m)	10 Ar
Power (kW)	25
Working distance (mm)	110
Chamber pressure (P_{sig})	5

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