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Laser processing of Ti composite coatings reinforced with hydroxyapatite and bioglass

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ABSTRACT

Composite coatings of titanium reinforced separately with hydroxyapatite (HAp) and bioglass (BG) were deposited on titanium substrate using Laser Engineered Net Shaping (LENS™). The microstructure, phase constituents, *in vitro* electrochemical, tribological and biological properties of these composite coatings deposited using different laser powers was studied. The composite coatings showed several reaction products such as $Ca_2P_2O_7$, $CaTiO_3$, $Na_2Ca_2Si_3O_9$ due to high temperature interaction of HAp and BG with Ti. The average top surface hardness of the Ti substrate was 148 ± 5 HV and that of the composite coatings was between 720 and 740 HV. As a result, the composite coatings exhibited significant increase in the *in vitro* wear resistance. The incorporation of HAp and BG in Ti increased the corrosion current, possibly due to the presence of residual stresses, but shifted the corrosion potential towards noble direction due bioactive reinforcements. *In vitro* proliferation of mouse embryonic fibroblast cells (NIH3T3) was found to be more on composite coatings than on titanium substrate demonstrating their superior cell-materials interactions.

1. Introduction

Due to their high strength, corrosion resistance and biocompatibility, titanium (Ti) and its alloys are most popular metallic biomaterials [1]. To improve bone cell − implant interactions and osseointegration of these metallic biomaterials, hydroxyapatite (HAp) coatings have been developed [2,3]. Among different techniques used to deposit HAp on metallic implants, plasma spraying is very popular commercially [4]. However, plasma sprayed coatings are prone to delamination, wear and tear thus generate undesirable debris [5–7]. The delamination is primarily due to lack of strong bonding and large difference in mechanical and physical properties of top HAp coating and the metallic substrate. Poor wear resistance is another important concern of Ti and its alloys although not required for all implants. However, some areas of the implants, such as interface between hip stem neck and taper bore of the femoral head, experience considerable amount of micromotions, where increase in the wear resistance of neck can significantly decrease the wear debris generation and improve *in vivo* life of the implants [8,9]. Generation of metal debris and metal ion release due to micro-motions could lead to implant loosening via osteolysis and metal sensitivity [10–13]. These problems can be addressed via depositing local composite coatings using lasers, which provide strong metallurgical bonding and controllable concentration of reinforcements [14–17]. Other important and beneficial characteristics of laser processing include strong bonding, absence of sharp interfaces, homogeneous and non-equilibrium microstructures with minimum dilution [17,18].

Addition of bioactive reinforcements, such as HAp and BG, could potentially improve cell-materials interactions of bioinert metallic implants, while simultaneously increasing the hardness. Similar observations have been reported with laser processed tricalcium phosphate (TCP) coatings on Ti and 316L stainless steel [16,19]. It is known that the BG chemically interact with physiological solution and rapidly form bioactive reaction layer compared to HAp. However, no reported literature is available on laser processing of BG coatings. Therefore, in this investigation, we have used Laser Engineered Net Shaping (LENS™) to deposit HAp and BG reinforced Ti composite coatings on Ti substrate. The aim was to investigate the influence of laser power and type of reinforcement on microstructural constituents and *in vitro* wear, corrosion, biocompatibility and cell-materials interactions.

2. Materials and methods

2.1. Coatings preparation

Ti powder (ATI Powder Metals, PA, USA) and laboratory

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Table 1
Laser process parameters used to prepare Ti composite coatings.

Sample I.D	Reinforcement	Laser power (W)	Scan speed (mm/s)	Energy density (J/mm^2)
BG200	Bioglass	200	10	40
BG300	Bioglass	300	10	60
HA200	Hydroxyapatite	200	10	40
HA300	Hydroxyapatite	300	10	60

synthesized HAp and BG powder (50–150 μm) were used in this study. A LENS™-MR7 (Optomec Inc. Albuquerque, NM) with 500W fiber laser (0.5 mm beam) and double powder feeder system was used to deposit ~ 0.5 mm thick HAp and BG reinforced Ti coatings on 3 mm thick rolled Ti substrate. The nominal composition (wt.%) of BG used in the present investigation was 57–60 SiO_2, 21–24 CaO, 9–11 Na_2O, 2–3 P_2O_5, 0.5–1.5 TiO_2 and 2–3 B_2O_3. The first hopper was filled with Ti powder and the second one with HAp powder or BG powder to prepare Ti composite coatings reinforced with HAp or BG, respectively. The powder feed rate was 1.7 g/min for Ti6Al4 V and it was 0.95 g/min and 0.60 g/min for HAp and BG, respectively. These are the minimum feed rates that could be used, with existing power feeders of LENS™-MR7, to enable powder transfer from the feeder to the deposition head and would result in Ti composite coatings with ~50 and 35% of HAp and BG, respectively. Our preliminary laser deposition of these composite coatings showed that sound coatings can be obtained at 200 W and 300 W laser power using 10 mm/s scan speed. Table 1 presents the details of samples and process parameters used in this investigation. All characterization and testing was performed on as-deposited coatings.

2.2. Microstructural analysis

The top surface and cross-section of the coatings were ground using a series of SiC grinding papers. Then the surfaces were polished with 1 μm and 0.05 μm suspension of Al_2O_3 powder on velvet cloth. The polished samples were cleaned and etched with Kroll's reagent. Microstructures of the coatings were observed using scanning electron microscope (ProX, Phenom-World BV, Eindhoven, Netherlands) and composition analysis was performed using energy-dispersive X-ray spectrometer (EDX). X'Pert Pro MPD diffractometer (PANalytical, USA), with 45 kV, 40 mA and Ni-filtered CuKα radiation, was used to determine the constituent phases of the coatings. Vickers microhardness measurements (W4303, ESEWAY, UK) were performed using1 kg load with a dwell time of 15 s.

2.3. In vitro corrosion and wear testing

Potentiodynamic polarization tests, conforming to ASTM G59, were performed in Hanks' balanced salt solution (HBSS), at room temperature, using a computer controlled potentiostat (SP300, Bio-Logic SAS, France). Sample surface was prepared following metallographic polishing procedure used for microstructural observation to ensure identical surface roughness. A saturated calomel electrode (SCE) and platinum mesh were used as reference electrode and counter electrode,

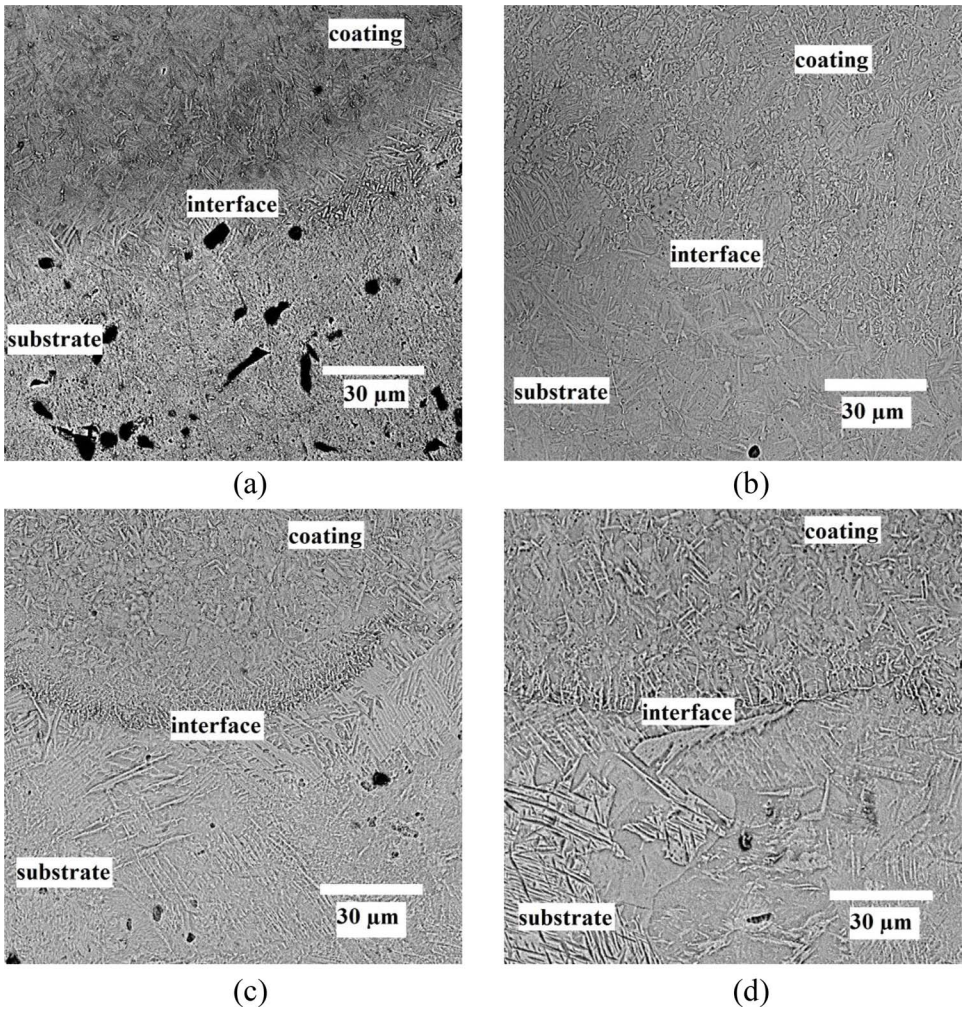

Fig. 1. Cross-sectional microstructures of composite coatings showing microstructural features and diffuse interface (a) BG200, (b) BG300, (c) HA200, (d) HA300.