Fabrication of compositionally and structurally graded Ti–TiO$_2$ structures using laser engineered net shaping (LENS)

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Abstract

Novel structures with functional gradation in composition and structure were successfully made in Ti–TiO$_2$ combination using laser engineered net shaping. The addition of fully dense, compositionally graded TiO$_2$ ceramic on porous Ti significantly increased the surface wettability and hardness. The graded structures with varying concentrations of TiO$_2$ on the top surface were found to be non-toxic and biocompatible. In addition, the higher wettability of surfaces with TiO$_2$ can enhance their ability to form chemisorbed lubricating films, which can potentially lower the friction coefficient against ultrahigh molecular weight polyethylene liner, thus reducing its wear rate. These unitized structures with open porosity on one side and hard, low friction surface on the other side can eliminate the need for multiple parts with different compositions for load-bearing implants such as total hip prostheses.

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1. Introduction

The high wear rate of ultrahigh molecular weight polyethylene (UHMWPE) liner used in traditional hip replacements is a cause of serious concern due to osteolysis. Osteolysis and aseptic loosening has been identified as major factors limiting the life of hip prostheses, with indications that fine UHMWPE wear debris [1,2], generated primarily at the interface between the femoral head and the acetabular cup, promotes this degradation. Thus, wear-particle-induced bone loss is one of the main limiting factors affecting the long-term stability of UHMWPE liner-based total hip replacements and other load-bearing implants [3,4]. Several attempts have been made to minimize the wear-induced osteolysis including the use of design modifications [5], UHMWPE property modification [6] and alternative bearing couples, such as metal-on-metal and ceramic-on-ceramic, eliminating the use of PE [7,8]. Design modifications can only change the contact stresses and related fatigue wear of the UHMWPE; modification of UHMWPE properties did not yield significant improvement in wear performance [9]. In addition, roughening and scratches on hard counterface of the femoral components can increase UHMWPE wear via adhesive and abrasive wear mechanisms [10,11]. An alternative and more effective solution is to modify the hard counter surface articulating with UHMWPE to reduce its wear and debris generation. Therefore, a hard counter surface providing low friction with UHMWPE and resisting roughening can reduce abrasive and adhesive wear, and thereby enhances the long-term stability and survival of load-bearing metal implants. Hard ceramic surfaces appear to accomplish this long-term performance goal most effectively [12] because of their higher wettability than metals/alloys. Among the ceramics TiO$_2$, Al$_2$O$_3$ and ZrO$_2$ have highly ionic character, therefore have higher wettability [13] than the passive oxide
films on stainless steels or CoCrMo alloys used for biomedical applications. Also, these passive oxide films on metals/ alloys can break off from the substrate during articulation and do not provide sufficient wear resistance or low friction against UHMWPE. It has been reported that lubricating compounds, such as water, readily chemisorbs to ceramics surface than to metals and these films can effectively reduce the friction coefficient and hence the wear of UHMWPE due to their lubrication characteristics [13–15]. Also, such adsorption activities were found to increase with ionic character of ceramics [13]. Therefore, a ceramic coating on biocompatible metals such as Ti can provide a favorable articulation surface with low friction coefficient and high wear resistance against UHMWPE to reduce its wear rate.

Recently there is a growing interest in the fabrication of novel structures to mimic multiple tissues and tissue interfaces on the same implant, such as implants with gradients in porosity and pore sizes that will allow on one side of the implant high vascularization and direct osteogenesis, while promoting osteochondral ossification on the other. In the current context, innovative designs such as functionally graded acetabular shells with open porosity on one side (in contact with the bone) to improve cell–material interactions and a hard ceramic coating on the other side (in contact with UHMWPE liner) to reduce liner wear, can significantly improve the implant’s in vivo life. While creating a hard/low friction ceramic surface on metal substrates seems plausible, there is a possibility of delamination or cracking due to the mismatch in elastic moduli, coefficient of thermal expansion and hardness between the ceramic coating and the metal substrate. Although functionally graded coatings (FGCs) can overcome such difficulties, it is difficult, if not impossible, to fabricate net shape implants/structures with spatial gradation in composition and structure (porosity) with conventional processing routes. Therefore, in this work we have used laser engineered net shaping (LENS™)—a solid freeform fabrication technique—to fabricate compositionally and structurally graded Ti–TiO2 structures with sound interface between the two materials and high surface hardness. Such gradient structures provide useful mechanical support for the wear-resistant, low friction exterior layers and minimize the likelihood of localized Hertzian failure during implant service. This paper focuses on processing, coating characterization and in vitro biocompatibility of these LENS™-processed functionally/structurally graded structures.

2. Materials and methods

2.1. Fabrication and characterization

Commercially pure titanium powder (Advanced Specialty Metals, Inc., NH) with particle size between 50 and 150 μm and 99% pure TiO2 powder (CERAC Inc., Milwaukee, WI) with particle size between 45 and 106 μm was used in this study. Gradient samples with 10 mm diameter were fabricated on a substrate of 3 mm thick rolled, commercially pure Ti plates using LENS™-750 (Optomec Inc., Albuquerque, NM) equipped with a 500 W Nd:YAG laser and double powder feeder system. The first hopper was filled with Ti powder and the second hopper with TiO2 powder. Gradient structures with 50%, 90% and 100% TiO2 on the top surface were made at 300 W laser power and 22.5 mm s−1 scan speed. These compositionally graded structures consisted of 100% Ti in the first 10 layers. The composition in the transition region of the gradient structure was varied from 100% Ti at the first layer to various concentrations of TiO2 at the top layer over 5–10 layers. The first 10 layers of Ti were made at 200 W to create ~30 vol % porosity, which can achieve stable long-term fixation due to bone cell in-growth through interconnected porosity [16]. The transition layers were made at 300 W to achieve fully dense transition/top layers. In the transition zone, the powder feed rate for TiO2 increased from 0 to 23.7 g min−1 over the number of transition layers. For Ti it was 17.5 g min−1 to start with and reduced to zero over the same number of layers. These compositionally graded structures with gradient porosity having open porosity on one side of the structure can improve cell–material interactions [16,17] and hard, low-friction coating on the other side can decreases the wear of UHMWPE liner. All samples were fabricated in a glove box containing argon atmosphere with O2 content less than 10 ppm to limit oxidation of alloys during processing.

Cross-sectional microstructures of the samples were examined using both optical and scanning electron microscopy (SEM). Constituent phases in the as-received TiO2 powder and in the top surface of graded coatings were identified using a Siemens D 500 Kristalloflex diffractometer with Cu Kα radiation. In order to track the compositional gradient across the deposit, a series of microhardness indentations were placed from one end of the deposit to the other end with neighboring indents being separated by 0.2 mm using Vickers microhardness tester (Leco, M-400G3) at 300 g load applied for 20 s. Top surface hardness was also measured, and an average of 10 measurements on each sample is reported.

2.2. Simulated body fluid (SBF) study

Bioactivity of compositionally/structurally graded Ti–TiO2 structures was evaluated by immersing in SBF with similar ionic composition as that of human blood plasma, and compared with that of laser-processed pure Ti control sample. The SBF solution is prepared by dissolving NaCl, KCl, NaHCO3, MgCl2·6H2O, CaCl2·2H2O, Na2SO4·10H2O and K2HPO4 into distilled water and buffered at pH 7.35 with tris-hydroxymethyl aminomethane (TRIS) and 1 (N) HCl at 37 °C [18]. The ion concentrations (mmol L−1) in SBF thus prepared was Na+: 142.0, K+: 5.0, Ca2+: 2.5, Mg2+: 1.5, HCO3−: 4.2, Cl−: 148.5, HPO42−: 1.0 and SO42−: 0.5. Samples were immersed in a glass vial containing 10 ml of SBF solutions and were kept under static conditions inside an incubator at 37 °C for 7 and 14 days.
The SBF solution was changed every 2–3 days for the duration of the experiment. All experiments were performed in duplicate, by running two independent glass vials simultaneously. After exposure, samples were washed with distilled water and then dried at 150 °C for 24 h. Surface feature of samples after SBF immersion were studied using a SEM. SBF-immersed samples were also analyzed by Fourier transform infrared (FTIR) spectroscopy (Nicolet 6700, Thermo Fischer Scientific) to identify functional groups of apatite precipitations on the surface.

2.3. Contact angle measurement

All the sample surfaces for contact angle measurements were ground using series of SiC grinding papers with various sizes up to 1200 grit. Samples were then polished on velvet cloth using 1 μm Al2O3 suspended in distilled water. Finally, just before testing, all the samples were ultrasonically cleaned in alcohol bath. This procedure ensured identical surface roughness and topography on all sample surfaces. Contact angles were measured using the sessile drop method with a face contact angle set-up equipped with a microscope and a camera. A 0.5–1.0 μl droplet of distilled water was suspended from the tip of the microliter syringe. The sample surface was advanced toward the syringe tip until the droplets made contact with the sample surface. Images were collected with the camera and the contact angle between the drop and the substrate was measured from the magnified image. All the measurements were carried out at 21 °C with a relative humidity of 21%.

2.4. Cell culture and morphology of osteoblastic precursor cell line 1 (OPC1)

All samples for cell culture test were sterilized by autoclaving at 121 °C for 20 min. In this study, the cells used were an immortalized, cloned OPC1, which was derived from human fetal bone tissue [19]. OPC1 cells were seeded on porous Ti and graded TiO2–Ti powders. However, severe cracking was observed in the structures with 100% TiO2 on the top surface and the cracking was reduced with decreasing TiO2 concentration. Therefore, further characterization and testing was not performed on the samples with 100% TiO2 on the top surface. Using optimized LENS™ processing parameters crack-free structures containing up to 90% TiO2 on the top surface were successfully fabricated with excellent reproducibility. Interface between porous Ti and graded TiO2–Ti top surface, shown in Fig. 2, also indicate complete melting of Ti and TiO2, ensuring sound interface without cracks or porosity. Also, no unmelted or partially melted powders were observed throughout the structure’s cross-section. This indicates small temperature fluctuations in the liquid metal pool due to changes in the composition across the sample cross-section. Large temperature fluctuations can result in non-uniform or inadequate intermixing of powders in the transition region of such graded structures [17]. In the present work, the small temperature fluctuations could be due to small difference between melting points of Ti (1668 °C) and TiO2 (1800 °C), and their laser absorption coefficients.

Top surface microstructural variation as a function of TiO2 concentration of graded structures is shown in Fig. 3. The top surface microstructures did not show clear contrast between Ti and TiO2 phases. However, it can be seen from Fig. 3a and b that the amount of Ti phase (phase with clear grain boundaries and grains with β needles) decreased with increasing TiO2 concentration. Lightly etched, fine TiO2 grains in the range of 6–8 μm (measured using linear intercept method) can be seen from Fig. 3b. Overall scale of the solidification structure in these graded coatings is very fine, reflecting the extremely high cooling rates, in the range of 103–105 K s⁻¹, associated with LENS™ process. This is a significant advantage of LENS™, as the slow cooling rates associated with other processing techniques often result in coarse-grained structures and results in poor wear resistance. The Ti phase in Fig. 3a is found to contain some high temperature β phase (needles). The retention of β phase at room temperature is attributed to the high cooling rates associated with laser processing. However, the amount of β phase observed in the present samples is considerably lower than observed in our earlier study [20] on LENS™-processed porous Ti, where a considerable amount of β phase is retained at room temperature. The lower amount of β phase in the present samples is presumably due to stabilization of α phase by the

3. Results and discussion

3.1. Microstructures and phase analysis

A representative cross-sectional microstructure of graded Ti–TiO2 structure is shown in Fig. 1. The Ti–TiO2 graded structures exhibited good bonding between individual layers without gross porosity, cracks or lack of fusion defects. This indicates that laser parameters used in the present work are sufficient to ensure complete melting and uniform mixing of TiO2 and Ti powders. All samples for cell culture test were sterilized by autoclaving at 121 °C for 20 min. In this study, the cells used were an immortalized, cloned OPC1, which was derived from human fetal bone tissue [19]. OPC1 cells were seeded on porous Ti and graded TiO2–Ti powders. However, severe cracking was observed in the structures with 100% TiO2 on the top surface and the cracking was reduced with decreasing TiO2 concentration. Therefore, further characterization and testing was not performed on the samples with 100% TiO2 on the top surface. Using optimized LENS™ processing parameters crack-free structures containing up to 90% TiO2 on the top surface were successfully fabricated with excellent reproducibility. Interface between porous Ti and graded TiO2–Ti top surface, shown in Fig. 2, also indicate complete melting of Ti and TiO2, ensuring sound interface without cracks or porosity. Also, no unmelted or partially melted powders were observed throughout the structure’s cross-section. This indicates small temperature fluctuations in the liquid metal pool due to changes in the composition across the sample cross-section. Large temperature fluctuations can result in non-uniform or inadequate intermixing of powders in the transition region of such graded structures [17]. In the present work, the small temperature fluctuations could be due to small difference between melting points of Ti (1668 °C) and TiO2 (1800 °C), and their laser absorption coefficients.

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oxygen present in top surface with varying concentrations of TiO₂. In addition, the ratio of β phase peak intensity to the α phase peak intensity found to decrease from 0.252 in the as-received powder to 0.102 in the graded structure with 50% TiO₂ on top surface. This indicates that the amount of β phase present in the as-received powder was reduced due to laser processing. The presence of β phase in the top surface of these samples was also confirmed by XRD study. Fig. 4 presents the XRD results of as-received powders and laser-processed gradient structures. All the peaks from top surface of gradient structures correspond to as-received powders of Ti (JCPDS file No. 011197) or TiO₂ (JCPDS file No. 881172).

In order to systematically track the compositional gradient across the deposit, a series of microhardness indent markers were placed from one end of the transition region to the other end. The hardness gradually increased with the increase in TiO₂ concentration as shown in Fig. 5. Gradual increase in the hardness from Ti towards the top TiO₂ coating validates the potential of LENS™ process in creating unique microstructural gradients across the compositionally graded surfaces/coatings, which are difficult to process using traditional manufacturing routes. The hardness of the top surface increased from 1102 ± 140 Hv to 1122 ± 116 Hv when the TiO₂ concentration at the top surface was increased from 50% to 90% in the coating. This indicates that the concentration of TiO₂ above 50% had little influence on the top surface hardness. These top surface hardness values are significantly higher than the average hardness of the laser-deposited Ti, which was 192 ± 14 Hv. Gradient coatings with only 50% TiO₂ in top surface showed ~474% increase in the surface hardness. The finer grain size, uniform microstructure and high hardness of this laser-processed gradient coating can potentially provide excellent wear resistance. Moreover, the porosity on the Ti side, which will be in contact with bone, can improve cell–material interactions [16]. It is anticipated that hard TiO₂ ceramic coating on the other side can decrease the wear of UHMWPE due to its higher wettability and chemisorbed lubricating films [13–15]. Therefore, these composi-
tionally/structurally graded Ti–TiO$_2$ structures could provide a favorable articulation surface with low friction coefficient and high wear resistance against UHMWPE reducing its wear rate.

3.2. SBF study

For comparison of bioactivity in terms of apatite-forming ability, laser-processed graded structures and Ti samples were immersed in SBF for 7 and 14 days. Fig. 6 shows surface micrographs of these samples after 14 days of immersion in SBF. It can be seen from Fig. 6a that laser-processed pure Ti control sample surface has low apatite-forming ability than graded surfaces with various concentrations of TiO$_2$ on top. Also, significant amount of apatite precipitation was noticed after 7 days on these compositionally graded surfaces. The FTIR results of these precipitates, shown in Fig. 7, indicate the presence of HPO$_4^{2-}$, PO$_4^{3-}$, OH$^-$ and CO$_3^{2-}$ groups. The enhanced apatite-forming ability of TiO$_2$ containing surface can be explained on the basis of several reported models for apatite deposition on the TiO$_2$ surface [21,22]. The Ti–OH groups formed on the TiO$_2$ film, upon immersion in aqueous solutions, act as preferential nucleation sites for apatite crystals and favor deposition/precipitation on the surface. Therefore, the TiO$_2$ in the graded structures surface enhances apatite formation.

3.3. Contact angle

While TiO$_2$ in the surface of graded structures greatly improved the apatite precipitation, it can also significantly alter surface properties like wettability and surface energy, which has strong influence not only on cell–material inter-
actions but also on the ability to form chemisorbed lubricating films. The contact angle between water and the Ti surface decreased from 62 ± 3° to 41 ± 4° due to TiO₂ in the surface of graded structures indicating that the Ti surface is more hydrophilic in nature. Lower contact angle also suggests higher surface energy of graded surfaces with varying TiO₂ concentrations. The higher hydrophilicity and surface energy of these surfaces improved the apatite-forming ability in SBF. Besides, the higher wettability of surfaces with TiO₂ can enhance their ability to form chemisorbed lubricating films thus lowering friction coefficient against UHMWPE. Similar observations on the increase of wettability and surface energy due to surface oxide layers have already been reported [23,24].

3.4. Cell–material interactions

Cell–material testing is focused on cytotoxicity analysis of these LENS-processed structures to confirm that LENS processing does not have any toxic influence to these structures. The higher wettability of TiO₂ containing surfaces found to influence the OPC1 cell attachment. Fig. 8 shows the morphology of OPC1 cells on graded Ti–TiO₂ structure surfaces after 7 days of culture. Flattened cells with little filopodia extensions were observed on laser-processed pure Ti samples. In contrast, the cells had numerous filopodia extensions on TiO₂ containing surfaces. Identical cell morphology was observed on the surface with varying concentrations of TiO₂ on the top surface, which spread and grew well on these sample surfaces. Enhanced osteoblast cell attachment and spreading on TiO₂ containing surfaces is attributed to the higher bioactivity and wettability of these surfaces compared to that of pure Ti surfaces. These in vitro results confirm that these compositionally and structurally graded samples are non-toxic and biocompatible even after LENS processing.

Graded structures fabricated in this work have the potential to replace conventional multi-piece hip implants by introducing monoblock structures. With these structures, acetabular shells can be designed with porosity in one side for bone tissue in-growth and the hard ceramic coating on the other side to reduce liner wear. This configuration can reduce the standard two-piece acetabular cup into a one-piece design. With further modification, the UHMWPE liner part can also be removed, making it a direct ceramic-on-ceramic implant. Such monoblock designs reduce the possibilities of osteolysis from polymeric debris and also make the surgical procedure easier.

4. Conclusions

Novel, unitized structures with porous Ti on one side and compositionally graded, hard TiO₂ surface on the other side have been fabricated using LENS™ process. Gradient structures with 50% TiO₂ in top surface showed a hardness of 1102 ± 140 Hv, which is approximately four times higher than the hardness of laser-processed Ti. Moreover, these gradient coatings decreased the contact angle by ~34% indicating their enhanced wettability, cell–material interactions and lubrication ability. Our results indicate...
that compositionally/structurally graded Ti–TiO₂ structures with 50% TiO₂ on top can provide a favorable articulation surface with low friction coefficient against UHMWPE reducing its wear rate.

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