

Laser induced hierarchical calcium phosphate structures

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Abstract

The surface properties of biomedical implant materials control the dynamic interactions at tissue–implant interfaces. At such interfaces, if the nanoscale features influence protein interactions, those of the microscale and mesoscale aid cell orientation and provide tissue integration, respectively. It seems imperative that the synthetic materials expected to replace natural hard tissues are engineered to mimic the complexity of their hierarchical assembly. However, the current surface engineering approaches are single scaled. It is demonstrated that using laser surface engineering a controlled multiscale surface can be synthesized for bioactive functions. A systematic organization of bioactive calcium phosphate coating with multiphase composition on Ti-alloy substrate ranging from nano- to mesoscale has been achieved by effectively controlling the thermo physical interactions during laser processing. The morphology of the coating consisted of a periodic arrangement of Ti-rich and Ca-P-deficient star-like phases uniformly distributed inside a Ca-P-rich self-assembled cellular structure with the presence of CaO, α -tricalcium phosphate, CaTiO_3 , TiO_2 and Ti phase in the coating matrix. The cellular structures ranged in diameter from 2.5 μm to 10 μm as an assembly of cuboid shaped particles of dimensions of $\sim 200 \text{ nm} \times 1 \mu\text{m}$. The multiscale texture also included nanoscale particles that are the precursors for many of these phases. The rapid cooling associated with the laser processing resulted in formation, organization and controlling dimensions of the Ca-P-rich glassy phase into a micron scale cellular morphology and submicron scale clusters of CaTiO_3 phase inside the cellular structures. The self-assembly of the coating into multiscale structure was influenced by chemical and physical interactions among the multiphases that evolved during laser processing.

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1. Introduction

Calcium phosphate (Ca-P) compositions are materials with excellent biocompatibility. In their bulk form, however, due to their inferior mechanical properties they are unsuitable candidates for applications involving direct replacement of hard tissues. However, Ca-P compositions deposited as coatings on a mechanically strong and biocompatible Ti-alloy substrate hold tremendous promise for exploitation in the bioenvironment. Typically, Food and Drug Administration (USA) approved plasma spray

techniques are adopted for coating implants with biocompatible materials. But the poor process control, irregular morphology, poor control of coating properties, and low adherence of the coatings often result in loosening of the implants in due course [1]. Based on this premise, laser assisted surface engineering is evolving as a alternative to the conventional plasma coating process and its suitability and potential as a tool in modifying implant surfaces have been already described in detail in Ref. [1]. Usually materials like hydroxyapatite (HA), zirconia or other bioglasses are coated on substrates like Ti alloys forming new chemical species, which would improve the biocompatibility [1]. On the other hand laser surface texturing to achieve three-dimensional structures at the micrometer and sub-micrometer scale has also been used for improving the biocompatibility of surfaces [1]. Moreover, with the

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advancement in characterization techniques and active collaborations between material scientists and biologists across the world, it has recently been realized that the surfaces of natural biomaterials are organized at multiscale levels and therefore synthetic replacement implants should also bear a close relationship with them, apart from just mimicking their chemistry. This stems from the fact that protein scale interactions are influenced at the nanoscale, the cell level orientation is involved with features at the microscale while the tissues interact with features at higher length scales [1]. In the present work, a concept involving simultaneous integration of coating and texturing operations was implemented to produce a textured coating using laser processing. Through modulation of the laser beam shaping optics and processing parameters (beam fluence and traverse speed), suitable thermal conditions were generated for the creation of a multiscale coating via melting and solidification of the precursor deposit.

2. Experimental work

Coupons (50 mm × 100 mm × 3 mm) of Ti-6Al-4 V alloy were cut from a large plate using Techcut10™ Allied High Tech Products Inc. The coupons were polished for a roughness of 0.5 μm. The starting powder of calcium phosphate tribasic, Ca₃(PO₄)₂ was obtained from Fisher Scientific. The coupons were washed in water and rinsed with acetone. Using an air spray gun the starting powder was mixed with a water based organic solvent and was sprayed onto these coupons to achieve a uniform thickness of 40 μm. A continuous wave Nd:YAG laser operating at a wavelength of 1064 nm was employed. In ambient air the samples were processed with 850 W power and processing speeds ranging from 0.021 m/s to 0.041 m/s. The laser beam at the focus was elliptical in cross section, being 5 mm × 1.5 mm in size. The processing was conducted by operating the laser beam in continuous mode such that with the given processing speed and beam size, it provided the beam residence (interaction) time of 45 ms at any given location on the sample. In order to examine the precipitation of HA as an indirect indication of biocompatibility of the modified surface, the laser surface modified samples were immersed in conventional simulated body fluid (SBF) for 14 days before being removed from the solution for scanning electron microscopy (SEM) and X-ray diffraction (XRD) analyses. SBF was prepared as per standard procedures reported in the literature [2]. The sample was placed in SBF maintained at a constant pH of 7.4 at 37 °C and refreshed every day for 14 days.

Using a Philips Norelco X-ray diffractometer, the starting powders as well as the coatings were characterized with Cu Kα radiation operated at 30 kV and 20 mA. The diffraction range was from 20° to 60° with a step increment of 0.02° and a count time of 1 s. Surface morphology was evaluated using a JEOL scanning electron microscope. Energy dispersive spectroscopy (EDS) for chemical microanalysis was performed in conjunction with SEM.

3. Results and discussion

3.1. Multiscale and multiphase microstructure

Calcium phosphate tribasic powder, a precursor, was pre-deposited at ambient temperature as a suspension in a water based organic solvent; therefore, as expected, it did not undergo any physical and chemical changes, which was verified using XRD and SEM analyses. It is, therefore, considered not necessary to include the corresponding XRD pattern and SEM image of the pre-deposited calcium phosphate coating prior to laser treatment. After laser processing, however, the samples were thoroughly observed by SEM to understand the surface characteristics. The morphology of the laser processed coating consisted of a periodic arrangement of star-like phases (A) uniformly distributed inside a self-assembled cellular structure (B) (Fig. 1a). The elemental analysis based on EDS data revealed that the star-like structure 'A' is Ti rich and Ca-P deficient (Fig. 1b) whereas 'B' is a Ca-P-rich region (Fig. 1c). Furthermore, XRD analysis (Fig. 1d) predicted the presence of CaO, α-tricalcium phosphate (TCP), CaTiO₃, TiO₂, along with Ti phase in the coating. The cellular structures ranged in diameter from 2.5 μm to 10 μm and they were an assembly of cuboid shaped particles of dimensions of ~200 nm × 1 μm. The assembly of these multiple phases into multiscale texture is more vividly realized in Fig. 2. It is worth noting that the multiscale texture also included nanoscale particles, labeled as 'C'. These particles can be the precursors for many other phases formed later. Although extensive efforts were made to assign the known phases (from JCPD files data base) to all peaks in the XRD pattern (Fig. 1d), a few peaks remain unidentified. Such a situation is very common, especially in material systems that involve several metallic and ceramic components with a possibility of formation of complex phases that are totally new and not referenced in the open literature. Furthermore, the evolution of such complex and previously unknown phases is highly likely to happen in a process such as laser processing that is often associated with near non-equilibrium or non-equilibrium thermodynamic conditions. Identification of such unknown phases could be a major effort and it was not the focus of this study. However, identification of such unknown phases could be considered if they are substantial in quantity and have a significant bearing on the end properties.

3.2. Morphological and chemical evolution

During laser interaction (laser fluence of 4.25×10^8 W s/m²) both the precursor calcium phosphate (melting point of TCP is 1550 °C) and part of the underlying substrate Ti-6Al-4V (melting point 1600 °C) were melted. As the laser processing was conducted in ambient atmosphere several oxide phases evolved, such as TiO₂ (melting point 1850 °C), CaO (melting point 2572 °C), CaTiO₃ (melting point 1992 °C), and P₂O₅ as indicated by the XRD

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