Laser Process Effects on Physical Texture and Wetting in Implantable Ti-Alloys

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Wetting is an important aspect for implantable biomaterials, as it affects the initial interaction with physiological fluids, which in turn dictates the protein adsorption, cell attachment, and tissue integration at the interface. In light of this in the present overview, surface engineering techniques based on laser processing of implantable titanium alloys for improved wettability and cell compatibility is discussed. Here three different laser processing techniques, laser interference patterning, continuous wave laser direct melting, and pulsed laser direct melting and the influence of each type of processing on the micro-texture evolution are studied. Finally, the effect of micro-textures on the wettability and thereby its in vitro bioactivity and in vitro biocompatibility is systematically discussed.

INTRODUCTION
Surfaces and Interfaces for Bone Tissue Engineering

The interface between the implanted biomaterial and the living tissue is the site of a variety of dynamic biochemical processes and reactions. These numerous atomic and molecular level events at the interface modulate the surface chemistry and morphology of the implant material, which in turn influences its long-term durability and compatibility inside the body. Under ideal situations, following implantation, a protein rich layer is supposed to be confirmed at the surface of an implant material as it further influences the cell attachment and tissue integration. The presence or the interaction of protein molecules depends on the wetting characteristic or the hydrophilicity of the implant material with the physiological fluids. The two most important factors that govern the wetting of the implant material with the physiological fluids are the surface chemistry and surface morphology of the implant material. Hence, there is a tremendous interest toward surface modification and effective design of such implantable materials so as to improve their hydrophilicity and thereby elicit a specific, desired, and timely response from the surrounding cells and tissues.

For bone tissue engineering applications, the most common design approach followed by various researchers is to mimic the functionality of the naturally occurring hierarchically organized hard tissue into the artificial implant material. It has been well understood that human bone is rich in calcium and phosphorous based hydroxyapatite (HA) phase at the nanoscale, and has a three-dimensional (3-D) extra cellular matrix (ECM) to support bone cells at the submicrometer scale. Hence, artificial biomaterials with biocompatible HA coatings on titanium based alloys, and engineered 3-D features at the meso-scale to support cells and tissue integration is becoming a reality. However, most of the surface engineering techniques used are “line of sight” methods: they either provide the appropriate surface chemistry (calcium and phosphorous based) or the 3-D topographic cue and lack in ability to achieve both simultaneously. Hence, in the present overview we demonstrate the laser-based surface engineering approach by which both an appropriate surface chemistry and regular 3-D topographic cues can be achieved simultaneously.

PULSED LASER SYNTHESIS OF TEXTURED Ca-P COATING

A pulsed laser is characterized by the short pulse duration (femtoseconds to milliseconds), high peak power, and intermittent delivery of the laser beam.
During the impact of such ultra-short pulses a fine layer of material is melted and then is vaporized at the surface, forming a vapor jet. This jet induces a recoil pressure and the liquid metal underneath is pushed toward the edges of the impact. After the end of the laser pulse the liquid metal solidifies and forms a crater on the surface of a metal. The presence of such a crater due to pulsed laser irradiation generates a physical texture on the surface of a material (schematically shown in Figure 1) and can be considered as a 3-D topographic cue for cell adhesion. The presence of short duration pulses also results in high cooling rate and thereby meta-stable phases suitable for bio-application. Their beneficial effects were explored in the samples pre-sprayed with HA powder suspended in a water-based organic solvent (LISI) and scanned under a Luminics JK701 model pulsed Nd:YAG laser. A metallurgical bonding at the coating/substrate interface and four different texture morphologies were obtained by varying the laser pulse frequency (10, 20, 30, and 40 Hz) and keeping the laser spot diameter (900 μm) and laser scan speed (50 cm min⁻¹) constant. These variations in frequency resulted in variations of 6%, 53%, 69%, and 76% crater overlap.

With an increase in pulse frequency there is an increase in crater overlap and hence varying surface textured morphology. Further, the 3-D morphological evolutions of the coatings (presented as insets in Figure 2) obtained using a confocal microscopic image indicate that the sample processed at 10 Hz possesses a relatively rough morphology as compared to the samples processed at higher frequencies. This is attributed to the fact that for the samples processed at higher frequencies the crater overlap was substantially high as compared to the sample processed at 10 Hz. This increased crater overlap resulted in re-melting of the major portion of the prior crater thereby smoothing the coating surface. The presence of such geometrically textured cues is expected to support bone cells and thereby induce bone ingrowth from the surrounding tissue.

The effect of surface morphology on its wetting behavior can be studied by the contact angle measurement of a simulated body fluid (SBF) subtended on these surfaces and by maintaining the SBF at 37°C and 7.4 pH. The composition and preparation of SBF solution was in accordance to References 11 and 12. The contact angle measurements carried out by a static sessile drop technique using a CAM Plus® contact angle goniometer (Cheminstruments, Inc. Fairfield, Ohio) indicated that all the laser-processed samples except for the sample processed at 10 Hz demonstrated an improved hydrophilic behavior as compared to the control Ti-6Al-4V (Figure 3a). Within the laser-processed samples, the sample processed at 40 Hz showed the maximum hydrophilicity to SBF with a contact angle of approximately 40°.

The improvement in hydrophilicity with increasing laser pulse frequency can be explained as per the schematic shown in Figure 3b. A practical rough surface is assumed to have a cosine profile with a Gaussian distribution and is character-

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\begin{align*}
\text{Equations} \\
\frac{w}{2} = \frac{\pi}{2 \sin \left( \frac{\theta}{2} \right)} \\
\cos \theta = \frac{w}{2\left(h^2 + \frac{w^2}{4}\right)^{1/2}} = \frac{1}{\sqrt{1 + \frac{4h^2}{w^2}}} \\
\cos \theta = \frac{1 - \phi_i}{R_f - \phi_i}
\end{align*}
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