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Review

Laser Surface Modification of Ti6Al4V Implants

Sumanta Mukherjee

Department of Mechanical Engineering, Indian Institute of Technology Kharagpur, Kharagpur, West Bengal, India, Pin 721302;
E-Mail: 10me90r15@iitkgp.ac.in
Tel.: +91-3222-281574

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Abstract: To improve the biocompatibility of implants, surface medication is a common practice. Depending on the surface medication process, the physical and/or chemical properties of the surface are altered, keeping the bulk properties same. The flexibility and wide application potential of laser as a surface modification tool gives it certain advantages over the traditional physical and chemical processes. The biocompatibility of Ti6AlV, already having suitable bulk physical properties, can be enhanced using different laser surface modification (LSM) techniques, as shown by many researchers. In this paper, the different routes of laser surface modification have been critically studied to find out their respective advantages and disadvantages. The LSM processes have been categorized into five major groups, namely laser surface cladding, surface modification using laser irradiation, direct laser texturing, laser lithography and laser additive manufacturing.

Keywords: Ti6Al4V; laser surface modification; orthopedic implants

1. Introduction

The alloy Ti6Al4V is very popular as orthopedic implant material because of its bulk mechanical properties. But as the biocompatibility of the implant depends on the surface properties also, it is a common practice to specially prepare the surface of the implant. Using different surface modification techniques, the physical and chemical properties of the implant surface are altered, without changing the bulk properties. Chemical etching, sand blasting and plasma-sprayed coating of Ca-P ceramics are most popular methods for commercial implants, though newer tools like laser are also under inspection for their flexibility and ability to process virtually all kinds of materials, including metals and ceramics.

In this paper, the LSM routes for implant surface modification have been studied for their respective advantages and disadvantages to find the suitable application zone for the processes. Some representative studies for each of the processes have been discussed.

2. Laser Surface Modification Processes

Laser Surface modification (LSM) covers a wide spectrum of surface modification routes, which can induce physical changes like changes in surface morphology and roughness, as well as chemical changes like changes in chemical composition.

For the convenience of discussion, the LSM processes have been categorized into five major groups depending on the modification mechanisms.

2.1. Laser Surface Cladding

In laser cladding, the implant surface is overlayed with a precursor material (or the powder is jet-sprayed), and the laser is used as the heat source to form a strong interfacial bond. Ca-P based ceramics are generally used as clad materials because of their biocompatibility. Moreover, such layers can act as biological barriers to the toxic ions of elements like Al and V.

The clad layer of Calcium Orthophosphate can be produced by two methods. In the first, the precursor powder of Calcium Orthophosphate itself. The powder is mixed with water/alcohol based organic binder, and the mixture is applied on the surface to be clad. After air drying the coating, laser melting is done to create a good bonding between the substrate and the coating. A schematic of the process is shown in fig. 1(a). Depending on the laser parameters, the surface properties and the bonding strength varies [1, 2]. In the second approach, the 'in-situ' route is used to synthesize the Calcium Orthophosphate [3, 4]. Cheap precursors like Calcium Carbonate mixed with Dicalcium Phosphate Dihydrate (DCPD) or Dicalcium Phosphate Anhydrous (DCPA) are used to prepare the pre-placed layer, which, during the laser cladding process, reacts to produce Hydroxyapatite. Evolution of reaction by-products like CO2 and water vapor results in development of porosity in the clad layer.

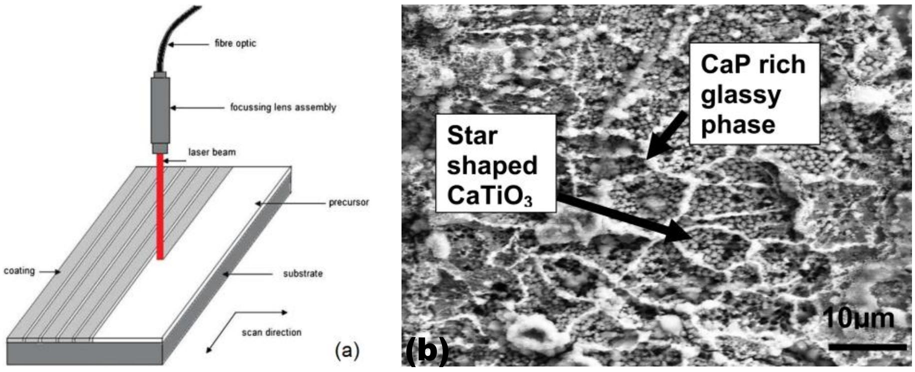


Figure 1. (a) Schematic of the Laser Cladding process [1]

(b) Composition of the clad layer [2]

There are some major issues with this process. Destabilization of Hydroxyapatite structure, leading to evaporation of significant portion of Phosphorus occurs at the high temperature associated with this process. Moreover, as formation of Tetracalcium Phosphate, Tricalcium Phosphate (both α and β),

$Ca_2P_2O_7$, CaO etc takes place in this process [2, 3], which gradually decomposes inside the body, leading to flaking off of the clad layer [5].

2.2. Surface Modification Using Laser Irradiation

When a pulsed laser beam falls on a surface, the high energy density causes some amount of the surface material to melt and evaporate. Depending on the energy density, the material may even get directly ablated, without going through the molten state. This mechanism of material removal creates nano-to-micron sized features on the surface, and the molten material resolidifies, changing the surface topography. Moreover, the fast cooling rate leads to formation of martensitic phase. In some cases, the laser is used to heat the surface just above the recrystalization temperature to change the phases present in the surface material.

Hao et al irradiated Ti6Al4V surface using a High Power Diode Laser to increase the wettability and Osteoblast response [6]. It was found that the surface irradiated with higher irradiation energy (1142 W/cm^2) showed higher wettability and biocompatibility. Probably melting and resolidification of the surface was the reason behind this.

Hallgren et al. [7] used kinoform to split a 3.5 mJ/pulse laser beam of Nd:YAG laser into an array, as shown schematically in fig. 2a. The laser irradiation produced 10 µm hemispherical pits with a pitch of 30 µm titanium dental implants (fig. 2b). The laser-patterned implants showed significantly more bon-to-implant contact in rabbit femur and tibia in a twelve week study.

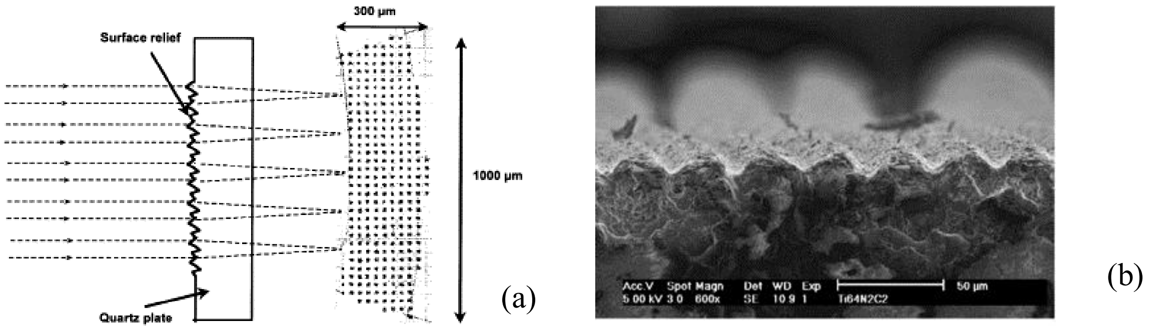


Figure 2. (a) Use of kinoform to split the laser beam for laser micromachining [7], **(b)** Heat affected zone in laser irradiated surface [9]

Laser surface irradiation process can be used to create geometrically defined surface features with controlled dimensions. It has been found that cell behavior can be influenced by the surface topography. When the depth and width of the microgrooves present on the surface are in a certain range, the cells tend to align themselves along the direction of the grooves. This phenomenon is called ‘contact guidance’. This preferential orientation of the cell growth can be utilized for more efficient bone regeneration on the implant surface, and the laser surface irradiation process can be used to prepare such surfaces [8].

In this process, only the ablated or evaporated material is removed, the molten material resolidifies. As a result, a major part of the thermally damaged material remains on the substrate. So, the material properties of the substrate get altered to a depth. The heat affected zone can be as high as 100-200 µm [9].

2.3. Laser Lithography

In lithographic process, a mask is used to selectively expose the surface to the laser irradiation. The masked areas remain intact, and materials from the unmasked areas are ablated. Depending on the mask designs, different patterns can be created on the surface.

Ricci et al [10] has studied microgrooves, having diameter 8-12 µm, on the Ti6Al4V surfaces. The microgrooves were created using a pulsed Excimer laser system and large area masking technique.

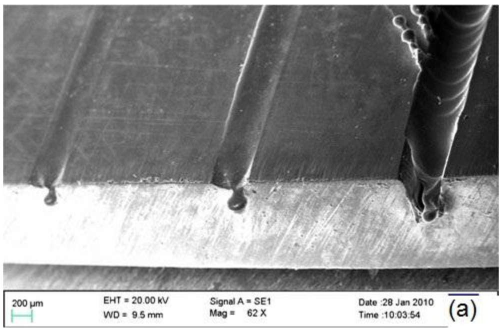
As the material removal mechanism is similar to the laser irradiation process, the issue related to the thermal damage of the bulk material, as mentioned earlier, is also there in this process also. The high energy ablation process may induce micro-cracks and create heat-affected zones within the micro-grooved structures [11, 12]. Moreover, the application of mask on complex surfaces is difficult.

2. 4. Direct Laser Texturing

In direct laser texturing, the laser beam melts the material and the material removal is by means of a co-axial assist gas jet. Typically Argon is used as the gas jet as it also acts as a shielding layer over the heated surfaces, preventing oxidation and/or nitridation. Using continuous laser beam, micro-grooves can be created on the surface, and pulsed laser can be used to create micro-pits.

Mukherjee et al [13] used a Yb Fiber laser to create microgrooves on the surface with an Argon gas jet of 1 bar pressure in excess to the atmospheric pressure (Fig. 3a). They varied the laser power, scan speed, duty cycle (the ratio of laser on time to the total cycle time) and frequency to get different 'secondary features' inside the grooves.

As the assist gas blows away the molten material from the surface, the thermal damage depth is minimal in direct laser texturing, which is a major advantage of this process, added to all the other advantages of the laser irradiation process. But similar to all other laser-related processes, this is also a line-of-sight process, so, enclosed surfaces are impossible to process using direct laser texturing.



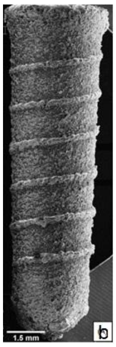


Figure 3. (a) Direct Laser Textured Microgrooves [13]

Figure 3. (b) Direct Laser Metal Sintered Implant, as-sintered [15]

2. 5. Laser Additive Manufacturing

Selective Laser Sintering (SLS) and Liquid Engineered Net Shaping (LENS) are the two laser additive manufacturing processes that can be used for manufacturing Ti6Al4V implants. In both the processes, Ti6Al4V powder is sintered using laser to build the implant layer-by-layer. The additive manufacturing processes offer excellent flexibility in implant design and the level of customization is unmatched. It is possible to manufacture highly porous and functionally graded scaffolds using the laser additive manufacturing routes.

Bandyopadhyay et al [14] created Ti6Al4V parts with porosity up to 40% using the LENS process, and it has been found that porous structures having 23-32% porosity have modulous equivalent to natural bone. The porous structures were found to accelerate the healing process in a 16 week study with rabbits.

The DMLS process was used by Traini et al [15] to manufacture isoelastic functionally graded scaffold, made of Ti6Al4V. They also found the elastic modulus of the sintered part to be significantly less than the solid Ti6Al4V, making the scaffolds more resistant to the ‘stress-shielding’ phenomena.

There are two major issues associated with the process, cost being the first. Secondly, being manufactured layer-by-layer, the side-surfaces are stepped, making them extremely rough. The material data sheet of the EOSINT M270 machine (EOS GmbH - Electro Optical Systems) specifies the roughness of the as-build surfaces to be as high as Ra 9 - 12 μm and Rz 40 - 80 μm [16]. So, the as-build parts are not suitable for use, and further post-processing is required.

3. Conclusions

Going through the basic mechanisms of the discussed routes, and the relevant studies conducted by researchers, it can be concluded that the family of the LSM processes can be used with great effect to functionalize the Ti6Al4V implant surfaces. Among the processes discussed above, Direct Laser Texturing shows some distinct advantages, such as

- Geometrically defined surface features with controlled size can be generated (similar to Laser Irradiation and Laser Lithography processes)
- Low HAZ (advantage over both Laser Irradiation & Laser Lithography)
- No foreign material is added during processing (advantage over Laser Cladding)
- Good surface finish (advantage over Laser Additive Manufacturing)

So, it can be concluded that though all the LSM routes have their own fields of application, the Direct Laser Texturing can be considered to be potentially most flexible and of highest importance. By controlling the assist gas flow apart from the laser parameters, this process can create highly functionalized surfaces.

Conflicts of Interest

The author declares no conflict of interest.

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