



# Surface modifications of titanium implants – The new, the old, and the never heard of options

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## Abstract

Successful implant osseointegration requires an ideal biochemical environment for safe integration into the jaw bone. To achieve better osseointegration, implant surface plays a vital role for the cellular level molecular interaction. Hence, various surface treatment options have been adopted as the latest course of action for the titanium (Ti) implants. This review throws a light on various methodologies of surface treatments and their pursuance on Ti implants, also the different responses observed by various surface designs and coatings.

## Introduction

In the past 20 years, the prosthetic rehabilitation option for patients with partially and completely edentulous arch has been taken over by dental implants. Clinical success of dental implant can be attributed to their early osseointegration. The beneficial combination of biocompatibility, mechanical strength, and chemical stability of pure titanium (Ti) and Ti alloys is highly documented and hence they can be used as standard materials in oral implantology. Branemark *et al.* discovered the concept of osseointegration, which changed the course of dentistry by introducing concept of oral implant in fixed treatment modality. Smooth surface and machined Ti implants have been used successfully in the field of implantology for past 50 years. Such implants have been tested on animal models by biochemical and histological evaluation, employing long term *in vivo* studies. Various surface modifications of implants which have been introduced are only to promote osseointegration with accelerated and stable bone formation.<sup>[1]</sup>

## Surface roughness of dental implants

Depending on the different surface treatments exposed onto the Ti, its surface roughness has been classified as micro-, macro-, and nano-roughness. Surface roughness not

only increases the implant stability while healing but also improves the osseointegration by inducing bone formation. Microroughness can be incorporated by threaded design and by producing macroroughness on Ti surface. To amplify the interlock formation between implant surface and the bone, microroughness within the range of 1-10  $\mu\text{m}$  should be added. The microrough surface on implant surface attained by immersing it for few minutes in a mixture of concentrated HCl and  $\text{H}_2\text{SO}_4$  above 100°C. The rate of osseointegration is influenced by the surface profile in the nanometer range as it helps in adsorption of protein and adhesion of osteoblastic cells. These methods use plasma spraying (PS), blasting with ceramic particles, anodization, and acid-etching.<sup>[2,3]</sup>

Implant surface quality has been classified by Albrektsson and Wennerberg into:

1. Mechanical,
2. Topographic, and
3. Physicochemical properties.

## Micron-scale surface topography and nanotechnology altering the surface reactivity

Implant to bone integration may be determined by nanoscale and micron-scale parameters of implant surface texture. When

implant topography is altered by nanoscale alterations, it affects the chemical reactivity, ionic, and biomolecular interactions between the implant and bone. Suggested advances are increased wettability, modified protein adsorption, and latent mineralization phenomenon.<sup>[2]</sup>

## Different Surface Treatments

### Classification

- Subtractive treatments
  - Machined
  - Sandblasted
  - Acid-etched surface
  - Dual acid-etching
  - Sandblasted and acid etched surface (SLA)
  - Laser treatment
- Additive treatments
  - Anodization
  - Fluoride surface treatment
  - Nanostructured surface
  - Spraying plasma
    - Ti
    - Hydroxyapatite (HA).
  - Coating sol-gel
  - Sputter deposition
  - Electrophoretic deposition
  - Biomimetic precipitation
  - Drugs incorporated.

#### *Machined surface (turned surface)*

The presence of crease, crinkle, and splotch by the device used for the manufacturing on the surfaces of machined implants provides mechanical interlocking, and it has been documented by scanning electron microscopic analysis. The morphology of non-treated implants (machined) enables the growth of osteoblastic cells into the grooves on the surface, which is a disadvantage. The machined implant surface is considered to be minimally rough. Machined implant surfaces have  $S_a$  values of 0.3-1.0  $\mu\text{m}$ . This feature requires a longer waiting time between surgery and implant loading.<sup>[4]</sup>

#### *Sandblasted surface*

Another approach for roughening the Ti surface consists blasting the implants with hard ceramic particles. Different surface roughness which produced on implant surface depends on the size of the ceramic. The surface roughness usually found to be anisotropic because of craters, ridges, and occasionally particles enclosed on the surface.

Other ceramic particles which were used are alumina, Ti oxide, and calcium phosphate. Alumina ( $\text{Al}_2\text{O}_3$ ) is frequently used as a blasting material. These particles hamper the process of osseointegration when released into the surrounding tissues, and physiological environment may decrease the excellent corrosion resistance of Ti implant.<sup>[5]</sup>

A maximum implant roughness of 1.5  $\mu\text{m}$  is required to attain maximum biologic response.<sup>[1,4]</sup>

### Acid-etched surface

Ti dental implant surface can also be roughened by etching with strong acids such as HCl,  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ , and HF. It produces micropits of 0.5-2 mm in diameter on Ti surfaces by immersing implants for few minutes in a mixture consisting of concentrated HCl and  $\text{H}_2\text{SO}_4$  which is heated above 100°C. Dual acid-etching accelerates the osteoconductive process, by directly forming bone on the surface of the implant, through fibrin and osteogenic cell attachment.

The oxide layer on the Ti surface can be removed by acid-etching, and the roughness is dependent on the bulk of material, surface microstructure, acid, and soaking time.<sup>[6]</sup>

When Ti reacts with fluoride ions, it forms soluble  $\text{TiF}_4$  species. Fluoride-treated Ti surface produced surface roughness as well as favorable osseointegration.

Chemical treatments also have the potential to improve implant anchorage in bone by rendering the implant surface bioactive. Nevertheless, mechanical properties of Ti can be reduced by chemical treatments. For instance, acid-etching can lead to hydrogen embrittlement of the Ti, creating microcracks on its surface that could reduce the fatigue resistance of the implants.<sup>[5,7]</sup>

### Dual acid-etched surface

By immersing Ti implants for few minutes in a mixture of concentrated HCl,  $\text{H}_2\text{SO}_4$  and heated above 100°C to produce microroughness on its surface and to enhance the osteoconductive process through the fibrin and osteogenic cell attachment, resulting in bone formation (dual acid-etching).

Advantage of this technique is that it produces high adhesion and enunciation of platelet and extracellular genes, which help in immigration of osteoblasts at the site and benefit osseointegration.<sup>[2,6]</sup>

### Sandblasted and acid-etched surface (SLA)

It is done by a process of blasting (large grit 250-500  $\mu\text{m}$ ) and by etching the implant surface with hydrochloric/sulfuric acid. It produces microtexture and results superior bone assimilation as related to the above-said methods.

This procedure creates a new hydrophilic surface (SLActive) and allows the SLActive to maintain a chemically active surface. Anions also can be added, which are taken from acids such as fluoride ions (when etched with hydrofluoric acid) into the oxide layer.

Studies have shown that SLActive implants produce a greater bone contact and stability at early healing phase (6 weeks) when correlated with SLA implants and fasten healing times.<sup>[2,6,7]</sup>

#### *Laser treatment*

The laser ablation technology develops microstructures on Ti implant surface which aids in osseointegration by increasing its

hardness, resistance to corrosion, and a large quality of purity with a definitive roughness and compact oxide layer. Biological studies have figured out; the importance of laser ablation on implant surface and chemical properties revealed that creased surface of implant is necessary to adapt osteoblast cell attachment and control its direction of ingrowth.

The advantages of this technique are that there is no chemical so better to use in manufacturing on routine basis. *In vivo* studies have showed a symbolic escalation in torque removal, long-term bonding to the bone, interface strength, and different fracture mechanisms.<sup>[8-10]</sup>

### Additive surface treatments

#### Anodized surface or oxidized surface

Anodization is a process by which oxide films are deposited on Ti implant surface by means of an electrochemical reaction. In this process, Ti surface to be oxidized plays as anode in an electrochemical cell with diluted solution of acids acting as the electrolyte.

Micro- or nano-porous surfaces can be formed by potentiostatic or galvanostatic anodization of Ti in strong acids ( $H_2SO_4$ ,  $H_3PO_4$ ,  $HNO_3$ , and HF) at high current density ( $200 A/m^2$ ) or potential (100 V). The result of the anodization is to thicken the oxide layer to more than 1000 nm on Ti.

The TiUnite surface (anodized surface) is a phosphate enriched and partially crystalline Ti oxide with wide opening on its surface. Anodized surfaces result in a strong reinforcement of the bone response in comparison to machined surfaces. Depending on the electrolyte distribution, various ions could be unified in the oxide layer, such as phosphorus, magnesium, and calcium. They are basically amorphous with crystalline grains of anatase.

At immediate implant placement, early molecular events of healing phase and osseointegration can be accentuated by phosphorus-containing anodized surface.

When an implant surface made of anodization and also by addition of calcium ions, it showed better osseointegration as well as removal torques were increased.<sup>[6]</sup>

Bone and implant interlocking through mechanical factors which occurs due to growth of bone into those surface openings and provides biochemical bonding.

Modifications to the chemical composition of the Ti oxide layer with the incorporation of magnesium, calcium, sulfur, or phosphorus lead to an uplifted torque removal values in comparison to other ions.<sup>[9]</sup>

#### Fluoride treatment

Ti implant surface showed to be very sensible to fluoride ions, and it forms soluble  $TiF_4$  when treated in fluoride solutions. This process on Ti heightens the osseointegration and uplifted osteoblastic differentiation when correlated with control samples (Ellingsen, 1995). Roughened implant surface by fluoride ion treatment also had a greater push-out forces and showed a significantly more advanced torque removal forces than the control implants.<sup>[2]</sup>

#### Nanostructured surfaces for implant dentistry

Nowadays, only a few nanoscale surface changes have been used to upgrade bone responses of clinical dental implants. The OsseoSpeed surface contains nanostructured details produced by  $TiO_2$  blasting followed by hydrofluoric acid treatment. Most of the osteoblastic gene expression was checked in cells attached to the nanoscale HF coated surface related to the micron-scale surface. This nanotopography is related with the elated levels of gene enunciation that reveal rapid osteoblastic differentiation.

IBAD or ion beam assisted deposition when used creates a thin film of ions over the implant surface by discharge of the chemical element of interest.<sup>[2,11]</sup>

Peculiar approaches applicable to layer Ti implants are:

- PS
- Sputter deposition
- Sol-gel coating
- Electrophoretic deposition
- Biomimetic precipitation.

### Roughening of Implant Surface by PS

PS coating is an optimized way to achieve a surface topography and morphology. The advantage of this technique is that these layers give implants a porous surface making easy for the bone to penetrate more easily. Bone to implant integration was found to be flashing and ultimate striking for rough surfaces within the range of 50-400  $\mu m$ . Ti and calcium phosphate (HA) can be added to the surface by spraying plasma.

#### Ti

These particles when envisioned on the implants where they condense and fuse together on its surface design a film which measures about 30  $\mu m$  thick. This layer must reach 40-50  $\mu m$  thickness to be homogeneous, smooth, and rigid. Average roughness of this layer should be around 7  $\mu m$ , which increases the surface area of the implant.<sup>[2]</sup>

#### HA coating

HA is one of the materials that may form a direct and strong binding between the implant and bone tissue. Kay *et al.* showed that for dental implant application, the coating of PSHA should be crystalline, and it offers compatible chemical and mechanical properties. Thomas<sup>[9]</sup> demonstrated an elevated bone formation and maturation around HA-layered implants in dogs when correlated with non-coated implants. Substrate alloys when modified with HA-coated layer, it resulted in increased corrosion resistance. The bone implant interface revealed to be better formed than with other implant materials and with enhanced mineralization. As the surface area of bone apposition to the implant increases, when related to uncoated implants, which may accentuate the load bearing capacity and biochemical bonding.<sup>[2]</sup>

### Sol-gel coated implants

This approach shows a straightforward and inexpensive method to apply thin layers with homologous chemical distribution onto substrates with complex design and bigger dimension. The advantage of this technique over bioactive ceramics is that it increases toughness of Ti alloys, biological affinity of HA, and mechanical strength. Layering Ti implants HA which is a bioactive material, result in accentuated early bone formation during healing face and improves implant bone integration.<sup>[2]</sup>

### Sputter deposition

Sputtering is a process, in which high-energy ions are discharged in a vacuum chamber to change the surface texture of a Ti implant surface.

### Radio frequency sputtering

This procedure involves the formation of thin films of CaP coatings on Ti implants. The choice of this technique could be due to formation of strong adhesive link/bond between the Ti and CaP ratio, and it also depends on crystallinity of the layered CaP.

### Magnetron sputtering

This process sustains the bioactivity of the coated HA by maintaining mechanical qualities of Ti. There will be formation of the TiO<sub>2</sub> layer at the bone and implant interface which establishes the strong bond due to the outwardly diffused Ti into the HA layer.<sup>[2]</sup>

### Biomimetic calcium phosphate coatings

In this method, Ti implant surface will have PSHA coating, which is inspired by the natural process of ion mineralization. There is surface modification by condensation of calcium phosphate apatite crystals onto the surface of implants from simulated body fluids formed a coating at room temperature.

It has been shown that such biomimetic coatings are more soluble in physiological fluids and resorbable by osteoclastic cells such as dentin materials than high-temperature coatings such as PSHA.<sup>[11]</sup>

### Biologically Active Drugs Incorporated Dental Implants

Incorporation of some osteogenic and antiresorptive drugs, such as bisphosphonate onto the implant surface, can be used appropriately in clinical cases with inadequate bone support.<sup>[2]</sup>

### Bisphosphonates

Bisphosphate-loaded implant surfaces have been reported to have improved implant osseointegration. With the incorporation of antiresorptive drugs, there will be increased density of bone around the implant. Studies using PSHA-coated

Ti implants engrossed in pamidronate or zoledronate showed a noticeable escalation in bone contact area. However, the major disadvantage will be present in the grafting and slow discharge of antiresorptive drugs on the surface of Ti implant.

### Simvastatin

Simvastatin could improve the enunciation of bone morphogenetic protein 2 mRNA that might promote bone formation. Clinical studies reported that statin use is associated with increased bone mineral density.

### Antibiotic coating

Antibacterial coatings on the surface of implants provide antibacterial activity to the implants themselves and serve as a possible way to prevent surgical site infections associated with implants.

Gentamicin in combination with HA when layered onto the surface; it will behave like a local prophylactic agent. Tetracycline-HCl treatment can be used as practical and efficient chemical method for decontamination and detoxification of harmed surface of implants.

Further, it hinders collagenase activity, accentuates proliferation of cells as well as attachment and bone healing. Tetracycline also enhances blood clot formation and its attachment and retention on the implant surface during the early healing phase and thus it accentuates osseointegration.<sup>[2]</sup>

### Conclusion

The endosseous dental implant has become a scientifically accepted and well-documented treatment for fully and partially edentulous patients because of their good biocompatibility and mechanical properties. The complex consequence of surface energy, composition, roughness, and surface texture of implant disposes its capacity to osseointegrate.

These surface modifications have encouraged the success rate of the implant therapy, in patients with poor quality of bone, and have notably decreased the healing period even though exact role of surface alterations has not understood. However, the development of these surfaces has been empirical, requiring numerous *in vitro* and *in vivo* tests. Most of these tests were not standardized, using different surfaces, cell populations, or animal models. Moreover, correlative clinical studies with various implant surfaces are notable achieved. The future of dental implantology should aspire at establishing surfaces with standardized surface chemistry of a Ti dental implant which implies to be assuring to enhance osseointegration.

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