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SURFACE TREATMENTS OF TITANIUM IMPLANTS

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Electrochemical and chemical surface treatments of titanium and titanium alloy implants include passivation, colour anodizing, alkaline "grey" anodizing, and electropolishing. The latter can be applied as a final treatment or prior to anodizing.

The main purpose of the electrochemical surface treatment, the colour anodizing,
has been over years the part identification. More and more surface functionalities brought by appropriate surface treatments are expected from the surface of dental and orthopaedic implants. The surface should warrant a good corrosion and wear resistance, anti-galling properties as well as an optimal biological response.

"The development of new surfaces can improve the overall performance of titanium implants, particularly in regard to the acceptance of the device by the body, the healing time after implantation and the long term integrity and stability of the biomaterial/body interface." [1]

Chemical and electrochemical surface treatments are well appropriated to modify the surface topography and to control the chemical composition of the outmost layer that plays a relevant role on the biological performance of the material.

Different surface processing methods are described in ref [2]. The chemical and electrochemical processes offered by Innosurf are briefly described hereunder:

PASSIVATION

Passivation treatments provide a controlled and uniformly oxidized surface state. The passivation leads to a dense and stable oxide film and improves corrosion resistance (decreases ion release). The passivation procedure involves nitric acid eliminating metallic contaminants from the surface. It has however practically no influence on the overall surface topography of titanium surfaces. The resulting layer of this chemical treatment is a TiO_2 film in a thickness of two to six nanometers.

BIOCOAT

(colour anodization)

By this process titanium is immersed into an electrolyte and connected as an anode leading to the formation of an oxide film at the surface

$$Ti \Rightarrow Ti^{2+} + 2e^-$$
$$2\ H_2O \Rightarrow 2\ O^{2-} + 4\ H^+$$

$$Ti^{2+} + 2\ O^{2-} \Rightarrow TiO_2 + 2\ e^-$$

The TiO_2 layer is highly resistive and the oxidation reaction will stop when the applied voltage is equal to the ohmic drop in the oxide film. The thickness of the oxide film is therefore a function of the applied voltage. This function is more or less linear and corresponds to 1.5 to 3 nanometers per applied volt. The proportionality constant depends namely on the alloy material, as well as on the electrolyte composition and temperature.

The oxide film acts as an interferential filter leading to beautiful colours varying in the same sequence as the rainbow when the voltage is increased. Typical thicknesses are in the range of 30 to 300 nanometers.

Biocoat applied directly and after electropolishing pretreatment

The main purpose of this electrochemical treatment is the part identification. However different topographical contrasts and therefore different surface functionalities can be obtained through mechanical and chemical pretreatments. A chemical etching is usually applied leading to a slight increase in roughness. On the other end a topographical levelling can be obtained when an electropolishing step is applied prior to the Biocoat treatment.

BIODIZE

(alkaline grey anodization)

This process is similar to the Biocoat however the specific electrolyte allows the formation of thicker TiO_2 layers in the range of micrometers. This

process has originally been developed for aerospace applications and corresponds to the AMS 2488c specifications. Improved wear and corrosion resistance as well as anti-galling properties are the main benefits of this coating for aerospace applications.

Titanium screws with the Biodize treatment

The alkaline anodization found large-scale applications for the treatment of orthopaedic implants. The advantages of this treatment are the following:

- The characteristic grey colour of Biodize is easily distinguishable from stainless steel
- anti-galling and wear resistance
- high strength to weight ratio, good fatigue properties and excellent corrosion resistance
- increase in fatigue strength of 15-20% due to the homogeneous surface treatment
- no introduction oh hydrogen or hydrogen embrittlement
- coating forms a penetrating layer rather than growth or "build-up" at the surface which results in no dimensional change
- The coating tends to level surface imperfections
- re-anodization is possible without need for stripping the original coating. Bare or machined areas will "heal" over and be indistinguishable from the original
- improvement to surface finish of greater than 50% is attained without special vibratory or burnishing methods
- the coating is continuous and does not flake off in highly stressed areas
- the coating is fully biocompatible to the human body

BIOBRIGHT

(electropolishing)

In this process titanium is immersed into an electrolyte and is connected as an anode leading to the dissolution of the titanium material. The electrolyte allows forming soluble compounds with the dissolved titanium. Furthermore the electrolyte develops a viscous film at the titanium-electrolyte interface providing a mass transport controlled dissolution reaction rate. Protruding parts dissolve faster than recesses leading to a levelling of the topographical contrast.

Efficient electrolytes based on perchloric acid are known since many years [2]. However, due to the explosive nature of this chemical compound, the process did not find large-scale industrial applications.

Innosurf applies a perchlorate free process, Biobright, where all danger of explosion is eliminated.

The removed layer of titanium is in the range of 5 to 30 micrometers. The thickness of the layer to be dissolved in order to reach a good levelling effect depends on the starting roughness of the material.

Electropolished agraphes with the Biobright process

Another beneficial effect of the electropolishing is the elimination of surface contaminants. Moreover since no hydrogen is involved in the preparation steps and since sharp scratches are levelled off, the fatigue resistance of the material increases.

CONCLUSION

In addition to part identification, the electrochemical and chemical treatments of titanium offer a range of surface functionalities related to modification of surface topography and control of chemical composition of the surface layer.

REFERENCES

[1] D.M. Brunette, P. Tengwall, M. Textor and P.Thomsen; Titanium in medicine; ISBN 3-540-66936-1; Springer Verlag 2001; Chap 5 p. 88

[2] id; Chap 8