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Review article

Biofunctionalization of titanium for dental implant

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Summary Surface modification is an important and predominant technique for obtaining biofunction in metals for biomedical use including dentistry. One surface modification technique is a process that changes the surface composition, structure, and morphology of a material, leaving the bulk mechanical properties intact. A tremendous number of surface modification techniques to improve the hard tissue compatibility of titanium have been developed. Hydroxyapatite layer, titanium oxide layer, and calcium titanate layer with various morphologies are deposited using electrochemical treatment including micro-arc oxidation. Also, surface modification layers without hydroxyapatite and calcium phosphate are chemically formed that accelerate bone formation. Other approach is the immobilization of biofunctional molecules such as poly(ethylene glycol) to the metal surface to control the adsorption of proteins and adhesion of cells, platelets, and bacteria. In the case of immobilization of biomolecules such as collagen and peptide, bone formation and soft tissue adhesion are improved.

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1. Introduction

Metals have a long history in the treatments of dentistry. However, metals are typically artificial materials and have no biofunction that leads to low attraction of metals as biomaterials. In this review, "biofunction" is defined not only as "inhibition of the non-specific adsorption of protein and adhesion of cells", but also as "enhancement of them". In addition, "metal-free" or "de-metallic" treatment is a trend in dentistry from the esthetic viewpoint. On the other hand, abrupt technological evolution on ceramics and polymers make it possible to apply these materials to medical devices the last three decades. In particular, excellent biofunctions of ceramics and polymers are expected to show excellent properties as biomaterials; in fact many devices consisting of metals have been substituted by those consisting of ceramics and polymers. In spite of this event, over 70% of implant devices in medical field including dentistry still consist of metals and this share is currently maintained, because of their high strength, toughness, and durability. Metallic biomaterials cannot be replaced with ceramics or polymers at present.

A disadvantage of using metals as biomaterials is that they are typically artificial materials and have no biofunction. To add biofunction to metals, surface modification is necessary because biofunction cannot be added during manufacturing processes such as melting, casting, forging, and heat treatment. Surface modification is a process that changes a material's surface composition, structure, and morphology, leaving the bulk mechanical properties intact. In addition, metals with biofunctions have been required in the recent past. In dentistry, dental implants require hard tissue compatibility for osseointegration and bone formation, soft tissue compatibility for adhesion of gingival epithelium, and antibacterial property for the inhibition of biofilm formation. These biofunctional properties consist of two conflicting properties: the inhibition and enhancement of protein adsorption or cell adhesion.

When a metallic material is implanted into a human body, immediate reaction occurs between its surface and the living tissues. In other words, immediate reaction at this initial stage straightaway determines and defines a metallic material's biofunction. With surface modification, biofunction of surface layer could be improved. For these purposes, many techniques for surface modification of metals are attempted on a research stage and some of them are commercialized. Reviews on surface modification of titanium (Ti) have already been published on sputter deposition [1] and electrochemical treatments [2]. In this review, surface modification techniques of Ti for dental implants are categorized and explained.

2. Surface modification techniques

In Table 1, surface modification techniques are categorized according to their processes and purposes. Major purpose of surface modification is to improve hard tissue compatibility or accelerate bone formation. Research to improve hard tissue compatibility involves two approaches based on the resultant surface layer: a calcium phosphate and titanium oxide layer with the thickness measured in micrometers and a surface-modified layer with the thickness measured in nanometers. Most of these processes have been developed since the 1990s. Fig. 1 shows the history of the surface treatment technique to improve hard tissue compatibility.

Surface property is particularly significant for biomaterials, and thus surface modification techniques are particularly useful to biomaterials. Dry process (using ion beam) and wet process (which is performed in aqueous solutions) are predominant surface modification techniques. In particular, electrochemical technique in the wet process is important near recently. Immobilization of bone formation factors such as bone morphological protein, BMP, or biomolecules such as collagen and peptide to metal surface is another technique to improve hard tissue compatibility. On the other hand, the immobilization of biofunctional molecules such as poly(ethylene glycol), PEG, to the metal surface to control the adsorp-

Table 1 Categorization of surface treatment techniques of metals for medical devices according to the process and purpose.

	Dry process	Electrochemical process Micro-arc oxidation	Chemical and hydrothermal process
Hydroxyapatite or calcium phosphate coating	Commercialized	Commercialized	Studied
TiO_2 or $CaTiO_3$ coating	Commercialized	Commercialized	—
Surface-modified layer formation [a]	—	—	Commercialized
Immobilization of functional molecules and biomolecules [b]	—	Studied	Studied

[a] Techniques forming a surface layer that enhances hard tissue compatibility, while the layer does not contain HA and calcium phosphate. See Section 5.
[b] Techniques immobilizing organic molecules including biomolecules to inhibit the adsorption of proteins or the adhesion of cells and to enhance them. See Section 7.