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IMPROVEMENT OF TITANIUM IMPLANT CHARACTERISTICS BY HYDROXYAPATITE COATING

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ABSTRACT

The mechanical properties of titanium and its alpha-beta alloys make them ideal implant materials. Hydroxyapatite coating substantially contributes to the improvement of these implants. This survey presents certain patterns of the combined use of hydroxyapatite with titanium and titanium alloys in dental and orthopaedic implantology. It demonstrates the advances of research on hydroxyapatite and its crystalline nanoparticles and reveals the advantages of and benefits from these coatings for further quality improvement of titanium implants.

Key words: titanium implant, hydroxyapatite properties, hydroxyapatite-coated titanium, hydroxyapatite deposition, osseointegration

INTRODUCTION

Titanium and its alpha-beta alloys possess mechanical properties that make them ideal implant materials. Because of light weight, high strength to weight ratio, low modulus of elasticity, excellent corrosion resistance and biocompatibility, good local spot weldability, easy shaping and finishing by numerous mechanical and electrochemical processes, these materials are widely used in dental implantology and restorative dentistry (3). On the other hand, there is rising evidence that coating with hydroxyapatite cement substantially improves these implants.

Characteristics of hydroxyapatite coatings on titanium implants

Clinical procedures place more stringent and tough requirements on the titanium surface necessitating its artificial treatments (5). Electrochemical techniques are simple and cheap methods of its modification. Anodic oxidation is the anodic electrochemical technique while electrophoretic and cathodic depositions are the cathodic ones. By anodic oxidation it is possible to obtain desired roughness, porosity and chemical composition of the oxide. At high voltages, it can improve the crystallinity of the oxide. The chief advantage of this technique is doping of the coating of the bath constituents and incorporation of these elements improves the properties of the oxide. Electrophoretic deposition uses hydroxyapatite powders dispersed in a suitable solvent at a particular pH. Under these operating conditions, these particles acquire positive charge and coatings are obtained on the cathodic titanium by applying an external electric field. These coatings require a post-sintering treatment to improve the coating properties. With the cathodic deposition, hydroxyapatite is formed in situ from an electrolyte containing calcium and phosphate ions. It is also possible to alter structure and/or chemistry of the obtained deposit. Nano-grained hydroxyapatite has higher surface energy and greater biological activity. Therefore, these coatings should be produced by cathodic deposition.

The effects of etching with hydrofluoric acid to change the surface morphology of titanium in cases of adhesion of calcium-deficient hydroxyapatite microspheres onto titanium are assessed (6). The coverage and the degree of adherence of the microsphere are evaluated by means of electron probe microanalysis. The etching at a hydrofluoric acid concentration of 0,10 mol/L cause the greatest adhesion. Changing the temperature between 303K and 323K shows a tendency towards increase of the degree of adherence.

Thermally induced liquid-phase deposition method is employed to produce a thin hydroxyapatite film on a titanium substrate in a metastable calcium phosphate solution (9). Prior to hydroxyapatite coating, the substrate is immersed in 5 M NaOH solution at 60^0C for 24 hours. An x-ray diffractogram indicates that the film deposited on the titanium substrate is composed of hydroxyapatite. Its amount augments with heating time increase. The uniform hydroxyapatite film can be formed by simple chemical and thermal treatments. This technique is useful for producing

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uniform hydroxyapatite coatings on complex-shaped and porous dental implants.

The survival of implants loaded 14 weeks after vertical ridge augmentation is evaluated within a 2-year prospective multi-centre study of 20 consecutive patients in three private centres (1). Nano-structured Mg-enriched hydroxyapatite is used as the only augmentation filler material. It is covered with a titanium reinforced extended polytetrafluoroethylene membrane (Gore-Tex). The amount of vertical bone gain, prosthesis and implant success, complications and radiographic marginal bone level changes are assessed at 12 and 24 months of prosthetic loading. Frequency resonance analysis of expressed values using implant stability quotient is performed at implant insertion, when definitive restoration is seated, and after 24 months of prosthetic loading. No patient drops out, all implants are clinically stable, and no prosthesis fails. Initial clinical evaluations show an average defect height of 4,1 mm. Complete bone filling of the regeneration volume is obtained in 19 out of 20 cases. The mean bone height gain is 5,6 mm. Radiographic assessments of inter-implant regenerated bone levels after 24 months of loading present a mean value of 1,0±0,48 mm. A statistically significant loss of peri-implant bone level occurs over time. The mean peri-implant bone levels are 0,3 mm at the time of prosthetic loading; 0,90 mm after 1 year, and 0,98 mm after 2 years. At implant placement, the mean implant stability quotient value is 49,3; at delivery of the final restoration it is 63,9 and after 2 years of loading it is 73,6. Vertical ridge augmentation around rough-surface implants using e-PTFE membrane and nano-structured Mg-enriched hydroxyapatite is successful even in cases with early loading.

Carbonated hydroxyapatite-coated titanium finds wide applications as bone substitute implant in dental surgery promoting osseointegration with a host bone and ensuring biocompatibility and bioactivity (8). Carbonated hydroxyapatite films are prepared on titanium substrates by pulsed laser deposition at different substrate temperatures (30^0C-750^0C). Their properties are studied by scanning electron and atomic force microscopy, energy-dispersive x-ray diffraction, and Fourier transform infrared spectroscopy. They are nearly stoichiometric with a Ca/P atomic ratio of 2,0-2,2. The films deposited between 30^0C-500^0C are about 9 micrometer thick, amorphous and of an average roughness of 60 nm. At 700^0C-750^0C, they are about 4 micrometer thick, show a finer surface morphology and an average roughness of 20 nm. At 750^0C, they are amorphous, whereas at 700^0C they are crystalline and textured along the (202) and (212) directions. The intrinsic hardness of the films increases with an increase in substrate temperature, being as low as 5 GPa at 30^0C and reaching a high value of 28 GPa at 700^0C.

The surface of commercially pure titanium dental implants coated with hydroxyapatite is characterized by plasma spray and biomimetic process (10). Scanning electron microscopy, Fourier-transformed infrared spectroscopy and x-ray photoelectron spectroscopy are performed. The plasma spray process generates a typical rough topography mainly consisting of hydroxyapatite. The hydroxyapatite coating produced by biomimetic process is partially dissolved in water and only a very thin layer of calcium titanate plus calcium phosphate and, probably, beta-tricalcium phosphate remains. In vitro test shows that both coatings can be considered bioactive. The modified biomimetic process is a simple and low-cost alternative to coat titanium with a high potential of in vitro application.

Orthopaedic applications of hydroxyapatite coatings on titanium implants

The effects of an electrochemically deposited nanohydroxyapatite coating on the bone bonding of sandblasted and dual acid-etched titanium implants are studied in 100 coated and uncoated titanium implants (3 mm in diameter, 10 mm long) (4). After 2, 4, 6, 8, and 12 weeks of bone healing, removal torque tests are performed to evaluate the interfacial shear strength of each implant type by means of an electron microscope equipped with an energy dispersive electron probe x-ray microanalyzer. The mean values for the electrochemically deposited nano-hydroxyapatite-coated implants are 39,6 Ncm at 2 weeks and 40,4 Ncm at 4 weeks while the corresponding values for the control implants are 21,1 Ncm and 24,1 Ncm. The values of these implants are by 87% higher than those of control implants after 2 weeks of healing ($p=0,015$). The mean values of both types of implants are, however, similar after 6, 8, or 12 weeks of healing. The electrochemically deposited nano-hydroxyapatite nanocrystal coating exerts a beneficial effect on interfacial shear strength during the early stages of bone healing.

The performances of commercially pure titanium screw dental implants, either uncoated, or coated with synthetic hydroxyapatite, are compared in vivo by electrophoresis (2). The histomorphometric patterns of hydroxyapatite coating are characterized by scanning electron microscopy. Besides analyses by energy dispersive spectroscopy and Fourier-transform infrared spectroscopy are applied. There is a significantly greater bone-implant contact of hydroxyapatite-coated implants ($p<0,05$) than of titanium implants. Comparison of bone content inside the screw implants shows no significant differences between both types of implants, although titanium ones have numerically higher percentage of bone content than hydroxyapatite-coated ones. The coating by electrophoresis is a valuable process to coat metallic implants with an osteoconductive material such as hydroxyapatite.

The effects of biomimetically and electrochemically deposited hydroxyapatite on the fixation of a porous titanium implant with bone tissue are examined (11). These implants belong to 3 groups: roughened, biomimetically deposited calcium-phosphorus, and electrochemically deposited hydroxyapatite. Removal torque tests and field-emission scanning electron microscopy observations are performed. The electrochemically deposited hydroxyapatite group shows significantly greater test values than do the other groups. The biomimetically deposited calcium-phosphorus group fails to increase the test values compared with the roughened one. Field-emission scanning electron microscopy demonstrates a greater amount of attached bone tissue on the electrochemically deposited hydroxyapatite-coated implant surface than that on the roughened and biomimetically deposited calcium-phosphorus-coated implant surfaces. The electrochemical hydroxyapatite coating contributes better to the fixation between bone and titanium implant.

The biologic effect in vivo of hydroxyapatite nanoparticle surface modification on commercially pure titanium or titanium alloy (Ti-6Al-4V) implants in progressive early bone-implant fixation is evaluated (7). Miniature cylindric titanium and Ti-6Al-4V implants are pretreated with dual acid etching and a subset is further modified with such nanoparticles using discrete crystalline deposition. The resultant implant surface topography is characterized by interferometry and scanning electron microscopy. After 4 days, 1 week and 2 weeks of healing, osseointegration is assessed by implant push-in tests or microcomputed tomography. Ti-6Al-4V samples are harvested at week 2, prepared for non-decalcified histology and subjected to bone-to-implant contact measurement. Discrete crystalline deposition treatment generates a complex surface morphology via the bonded hydroxyapatite nanoparticles. The amplitude and spatial, hybrid, and functional surface roughness parameters measured at the micron and submicron levels do not depict any topographic differences between the dual acid etching and the discrete crystalline deposition-modified titanium implants. Push-in values of dual acid etching titanium and Ti-6Al-4V implants sharply increase at week 1 followed by a plateau at week 2. Discrete crystalline deposition titanium and Ti-6Al-4V implants show similar sharp increases at week 1, however, these values continue to increase at week 2. The surrounding bone architecture evaluated by microcomputed tomography and the bone-to-implant contact ratio does not correlate with the biomechanical implant osseointegration measurement. Early osseointegration is more sensitively regulated by nanoscale surface characteristics.

CONCLUSION

Further comprehensive experimental and clinical investigations of hydroxyapatite coatings on dental titanium implants will promote the broader applications of these suitable biomaterials in everyday practice.

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