Biomaterials for Dental Implants: An Overview

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ABSTRACT

The goal of modern dentistry is to restore the patient to normal contour, function, comfort, esthetics, speech and health regardless of the atrophy, disease or injury of the stomatognathic system. As a result of continued research in treatment planning, implant designs, materials and techniques, predictable success is now a reality for the rehabilitation of many challenging situations. The biocompatibility profiles of synthetic substances (biomaterials) used for the replacement or augmentation of biologic tissues has always been a critical concern within the health care disciplines. For optimal performance, implant biomaterials should have suitable mechanical strength, biocompatibility and structural biostability in physiologic environments. This article reviews the various implant biomaterials and their suitability of use in implant dentistry.

Keywords: Biomaterial, Biocompatibility, Biostability, Biomimetics, Augmentation.

INTRODUCTION

Biomaterials are those materials that are compatible with the living tissues. The physical properties of the materials, their potential to corrode in the tissue environment, their surface configuration, tissue induction and their potential for eliciting inflammation or rejection response are all important factors under this area. The biomaterial discipline has evolved significantly over the past decades. The goal of biomaterials research has been and continued to develop implant materials that induce predictable, control-guided and rapid healing of the interfacial tissues both hard and soft.¹

The most critical aspect of biocompatibility is dependent on the basic bulk and surface properties and biomaterials. Materials used for fabrication of dental implants can be categorized in two different ways:

- 1. Chemical point-metals, ceramics
- 2. Biological point—biodynamic materials: biotolerant, bioinert, bioactive

Biomaterials, regardless of use, fall into four general categories: Metals and metallic alloys, ceramics, synthetic polymers and natural materials. Metals and metal alloys that utilize oral implants include titanium, tantalum and alloy of

Ti-Al-Va, Co-Cr-Mb, Fe-Cr-Ni. These materials are generally selected on basis of their overall strength properties.

Bioinert materials allow close approximation of bone on their surface leading to contact osteogenesis. These materials allow the formation of new bone on their surface and ion exchange with the tissues leads to the formation of a chemical bonding along the interface bonding osteogenesis.

Biotolerant are those that are not necessarily rejected when implanted into living tissue. They are human bone morphogenetic protein-2 (rh BMP-2), which induces bone formation *de novo*.

Biomimetics are tissue integrated engineered materials designed to mimic specific biologic processes and help optimize the healing/regenerative response of the host microenvironment.

Bioinert and Bioactive materials are also called osteoconductive, meaning that they can act as scaffolds allowing bone growth on their surfaces.

FACTORS AFFECTING IMPLANT BIOMATERIAL

Factor affecting biocompatibility includes chemical, mechanical, electrical and surface specific properties.^{2,3}

Chemical Factors

Corrosion may be defined as the loss of metallic ions from the surface of a metal to the surrounding environment. There are three basic types of corrosion: General, pitting and crevice.

General Corrosion

General corrosion occurs when a metal is immersed in an electrolyte solution. Positively charged ions from the metal are transferred to the liquid electrolyte and the metal transports the negatively charged electrons. This migration continues until the potential difference between the metal and electrolyte are great enough to prevent more ions from entering solution or electrons from being transferred, at which equilibrium point is achieved.

Pitting Corrosion

Pitting corrosion occurs in an implant with a small surface pit placed in a solution. Such an implant exhibits two different surface conditions. When the metal near the pit dissolves or loses positive ions from its surface, the associated negative charge from the liberated electrons must be dissipated through the metal of the implant. This type of corrosion can proceed very rapidly, actively attacking metallic implants if proper material and surface conditions do not exist. This corrosion type is called pitting corrosion.

Crevice Corrosion

Crevice corrosion that occurs around bone-implant interface or an implant device where an overlay or composite type surface exists on a metallic substrate in a tissue/fluids environment with minimal space, little or no oxygen may be present in the crevice. When metallic ions dissolve, they can create a positively charged local environment in the crevice, which may provide opportunities for crevice corrosion. Thus, the selection of metals and alloys for biomaterials depends on an understanding of corrosion and biocorrosion phenomena. All metals ionize to some extent, normally decreasing with increasing neutrality of the metallic solution.

Surface Specific Factors

Events at the Bone-Implant Interface

The performance of biomaterials can be classified in terms of:

- 1. The response of the host to the implant.
- 2. The behavior of the material in the host.

Material response: The event that occurs almost immediately upon implantation of metals, as with other biomaterials, is adsorption of proteins. These proteins come first from blood and tissue fluids at the wound site and later from cellular activity in the interfacial region. There is ample literature that describes oxidation of metallic implants both *in vivo* and *in vitro*. Although metallic implant biomaterials were originally selected because of their stable oxide films, it is appreciated that the oxide surfaces still undergo electrochemical changes in the physiologic environment. Furthermore, surface analytic studies show that the chemical composition of the oxide film changes by incorporating calcium, phosphorus and sulfur.

Another consequence of these events is the release of metallic ions into tissues. These corrosion by-products accumulate locally but may also spread systemically. Significantly elevated metal contents have been measured both in periprosthetic tissues in the serum and urine of patients with orthopedic implants.

Host response: The host response to implants placed in bone involves a series of cell and matrix events, ideally culminating in tissue healing, leading to intimate apposition of bone to the biomaterial, i.e. an operative definition of osseointegration. For this intimate contact to occur, gaps that initially exist between bone and implant at surgery must be filled initially by a blood clot, and bone damaged during preparation of the implant site must be repaired.

Morphologic studies have revealed the heterogeneity of the typical bone-implant interface. One feature often reported is the presence of an afibrillar interfacial zone, comparable to cement lines and lamina limitans. Although its thickness and appearance vary, this zone forms regardless of the type of biomaterial implanted, including CpTi, stainless steel and hydroxyapatite.

Osteoblasts, osteoid and mineralized matrix have been observed adjacent to the lamina limitans suggesting that bone can be deposited directly on the surface of the implant, extending outward from the biomaterial. Thus, bone formation in the periprosthetic region occurs in two directions: The healing bone approaches the biomaterial, but also bone extends from the implant towards the healing bone. In vitro studies, bone cell culture models are employed increasingly often to study bone-biomaterial interactions. Most of the cultures have utilized osteoblastic cells with only a few using osteoclastic cells. It is known that bone from different sites, developmental ages and types show variability. An important consideration, however, is that the information obtained can indeed reflect in vivo events. For example, in vitro and in vivo models have shown formation of a cement line-like layer and appropriate organization of mineralized matrix during culture on various substrates. Understandably, because of the complexities of the in vivo environment, the bone-implant interface has not yet been fully characterized. The heterogeneity and patchy immunolabeling observed in morphologic studies suggest that even though several biomolecules have been identified at the interface, they are not likely the ones present.

Biomolecules also have essential roles in directing bone response to the implant. Further work is needed to identify them and determine their functions at the interface.

Controlling the Bone-Implant Interface by Biomaterials Selection and Modification

Different approaches are being used in an effort to obtain desired outcomes at the bone-implant interface. Many would accept the promise that an ideal implant biomaterial should present a surface that will not disrupt or even enhance the general processes of bone healing regardless of implantation site, bone quantity and bone quality.

Electrical Factors

Physiochemical Methods

Surface energy, surface charge and surface composition are among the physiochemical characteristics that have been altered with the aim of improving the bone-implant interface. Glow discharge has been used to increase surface free energy, so as to improve tissue adhesion. Increased surface energy does not selectively increase the adhesion of particular cells or tissues, it has not been shown to increase bone-implant interfacial strength. Although short-term clinical results have been encouraging, dissolution of coatings as well as cracking and separation from metallic substrates remain a concern with hydroxyapatite coatings.

Morphologic Methods

Alterations in biomaterial surface morphology and roughness have been used to influence cells and tissue responses to implants. Porous coatings were originally developed with the rationale that mechanical interlocking, bone ingrowth would increase fixation and stability of the implant. In addition to providing mechanical interlocking, surfaces with specially contoured grooves can induce contact guidance whereby the direction of cell movement is affected by the morphology of the substrate.

Concerning surface roughness and its effects, there is a large but inconclusive literature on the biologic and clinical effects. Using *in vitro* cell culture systems all the authors have not come to the same conclusions about the role of surface roughness. Cochran et al reported that human fibroblast and epithelial cell attachment and proliferation *in vitro* were affected by surface characteristics of titanium. Overall, these *in vitro* animal and clinical studies did not yield compelling conclusions about the role of surface to bone response at the interface.

Biochemical Methods

Biochemical methods of surface modification offer an alternative or adjunct to physiochemical and morphologic

methods. Biochemical surface modification endeavors to utilize current understanding of the biology and biochemistry of cellular function and differentiation.

The goal of biochemical surface modification is to immobilize proteins, enzymes or peptides on biomaterials for the purpose of inducing specific cell and tissue responses, or in other words to control the tissue-implant interface with molecules delivered directly to the interface. One approach for controlling cell-biomaterial interactions utilizes cell adhesion molecules. Since plasma and extracellular matrix proteins include fibronectin, vitronectin, Type-I collagen, osteogenin and bone sialoprotein. Research has also shown that RGD-containing peptides promote cell attachments.

A second approach to biochemical surface modification uses biomolecules, which demonstrated osteotropic effects. They have effects ranging from mitogenicity (interleukin growth factor-i, FGF-2 and platelet-derived growth factor-BB) to increasing activity of bone cells, which enhances collagen synthesis for osteoinduction.

MECHANICAL PROPERTIES

Important mechanical properties of biomaterials that must be considered in dental implant fabrication are:

- 1. Modulus of elasticity
- 2. Tensile strength
- 3. Compressive strength
- 4. Elongation
- 5. Metallurgy.

Modulus of elasticity: An important property of any biocompatible material is its modulus of elasticity (E), which represents elastic response to mechanical stress. The forces (F) and stresses within bone that result from loading an implant, balance the effect of the externally applied forces of occlusion or muscle action. These forces may establish a condition of static equilibrium. When these forces are not in equilibrium, the implant and bone deform or undergo mechanical strain. In elastic deformation, the implant and bone regain their original dimensions after the removal of force. In plastic deformation, the original dimension is altered permanently after the removal of the applied force. In this case, the properties of the material are such that a desired extent of permanent change of original dimension can be achieved while maintaining metallurgic and clinical integrity.

Tensile or Compressive forces (stresses): This force when applied to a biomaterial or bone cause a change of dimension (strain) that is proportional to the elastic modulus.

Elongation: The magnitude of the moduli of elasticity can provide a direct measure of the degree and relative movement at the interface that can be expected. Both the bone and the implant deform (strain) as a result of forces applied to either one. Physiologically, this relative movement in part determines the health or pathologic state of interface components and influences the surrounding tissue integration.

Metallurgy: The metals used in implant fabrication are an important consideration. Grains often called crystals can be of various geometric shapes. They exhibit crystallographic orientations that are a result of their formation, geometric shape and location within the bulk structure. Metals can be coined or squeezed into desired shapes when sufficient ductility exists, such that relative grain rearrangement occurs without disrupting integrity.

Coining is the process of shaping a metal in a mold or die especially by stamping. In the early 1970s, research by Matarese and Weiss solved this problem leading to fabrication of first coined endosteal dental implants. The coining process permits geometrically precise and planned modifications of grain size and orientation. This reduces metal fatigue over longer-term cyclic loading and promotes ease and increased safety during insertion adjustments to follow bone anatomy and to establish intraoral parallelism for prosthodontic restorations.

METALS AND ALLOYS

Most of the dental implant systems are constructed from metals or alloys. These include titanium, tantalum and alloys of aluminum, vanadium, cobalt, chromium, molybdenum and nickel. These materials are generally selected on the basis of their overall strength. The precious metals often used for restorations, such as gold, platinum and their associated casting alloys are less frequently used for dental implants.

Titanium

Metals as biomaterials have been increasingly used in various devices or structures used in contact with or within the biological system, like in orthopedics, dental and cardiovascular applications. The evolution of titanium (Ti) as biomaterial for medical and dental uses has dramatically increased in the past few years because of titanium's excellent biocompatibility, corrosion resistance and desirable physical and mechanical properties. Historically, titanium was discovered in 1789 by Wilhelm Gregor.⁴ The industrial utilization of Ti, however, started only about 60 years ago when it was used for the aerospace and defense industries, for which the metal's high strength and light weight offered solutions to many design problems for aircraft engines.⁵ Dr Wilhelm Kroll invented useful metallurgical processes for the commercial production of titanium metal, therefore, he is known as the Father of Titanium Dentistry.³ He successfully developed the deoxidization process of titanium tetrachloride through a reduction procedure with

General Properties of Titanium

Titanium is in its metallic form at ambient temperature, it has a hexagonal close-packed crystal lattice (α phase), which transforms into a body-centered cubic form (β phase) at 883°C, the melting point is 1,680°C. The strength, rigidity and ductility in pure form are comparable to those of other noble or high noble alloys commonly used in dentistry.^{7,8} Commercially pure titanium is available in four grades (1-4), according to American Society for Testing and Materials (ASTM), which vary according to the oxygen (0.18-0.40 wt%), iron (0.20-0.50 wt%) and other impurities. Other impurities include nitrogen (0.03-0.05 wt%), carbon (0.1wt%) and hydrogen (0.015wt%). Grade 1 is the purest and softest form, which has moderately high tensile strength.⁹ The environmental resistance of titanium depends primarily on a thin, tenacious and highly protective surface oxide film. Titanium and its alloys develop stable surface oxides with high integrity, tenacity and good adherence. The surface oxide of titanium, if scratched or damaged, immediately reheal and restore itself in the presence of air or water. The protective passive oxide film, which is mainly TiO₂ is stable over a wide range of pH, potentials and temperatures, and is specially favored as the oxidizing character of the environment increases.

Titanium, because of this protective coating, generally resists mild reducing, neutral and highly oxidizing environments up to reasonably high temperatures. It is only under highly reducing conditions that oxide film breakdown and resultant corrosion may occur. These conditions are not normally found in the mouth.⁵ The temperature dependant allotropic phase transformation from hexagonal close packed α phase to body centered cubic β phase at 885°C allows four different phase combinations of titanium alloys to be commercially available. These are α , near α , β and $\alpha\beta$. Aluminum, carbon, gallium, oxygen, nitrogen and tin are commonly added α stabilizers and nickel, copper, palladium, vanadium are β stabilizers added to $\alpha\beta$ and β phase alloys. Most commonly used alloys in dentistry are Ti-6Al-V, Ti-30Pd, Ti-20Cu, Ti-15V and Ti-6Al-4V.¹⁰⁻¹⁴

Corrosion

Titanium has long been successfully used as an implant material. Stable TiO_2 surface layer with a thickness of approximately 10 nanometers separates the reactive Ti from the electrolyte, thus generating high corrosion resistance. Titanium, however, is as corrosive as many other base metals under mechanical stress, oxygen deficit or at a low pH level. Long-term studies and clinical observations establish the

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fact that titanium does not corrode when used in living tissue, however, galvanic coupling of titanium to other metallic restorative materials may generate corrosion.^{15,16} Hence, there is a great concern regarding the material for superstructures over the implant. Moreover, self-formed protected oxide film on titanium can be affected by excessive use of the commonest preventive agents in dentistry, prophylactic polishing and topical fluoride applications. Fluoride contained in commercial mouthwashes, toothpaste and prophylactic gels are widely used to prevent dental caries or relieve dental sensitivity or for proper oral cleaning after application of normal brushes with toothpaste. The detrimental effect of fluoride ions on the corrosion resistance of Ti or Ti alloys has been extensively reported. Fluoride ions are very aggressive on the protective oxide formed on Ti and Ti alloys.¹⁷⁻²¹

Other Properties

Titanium is one of the metals that can be coupled with other metals without fear of losing its passivity. When coupled with metals of greater corrosion potentials it may corrode by the mechanism of galvanic corrosion. When coupled with metals, they remain passive and a stable combination is produced. It would therefore be wise to avoid metals that are not strongly passive, such as stainless steel. This should also be taken into consideration when selecting surgical instruments for the placement of titanium implants.

Selecting an Implant^{22,23}

Clinical evidence documents that all six commercially available dental implant biomaterials have exhibited excellent biocompatibility and tissue responses. None of the Ti-based materials have proved to be more biocompatible than any other group. Factors such as implant design, size and material strength should be determined in implant selection for a particular patient. If a patient has a history of parafunctional habits, the clinician should choose an implant made of Ti alloy rather than Cp grade I titanium. In addition, small diameter implants placed within thin walls indicate the need for high strength materials.

Tissue Response

The most commonly used biomaterials for dental implants are metals and their alloys namely commercially pure (CP) titanium and Ti-6A-14V, which are most commonly used as endosseous implants, whereas Co-Cr-Mo are most oftenly used as subperiosteal implants.

CpTi and Ti alloys are low-density metals that have chemical properties suitable for implant applications. Ti has poor shear strength and wear resistance making it unsuitable for articulating surface or bone screw application. Ti has high corrosion resistance attributed to the surface oxide layer that creates a chemically nonreactive surface to the surrounding tissue. Both elastic modulus and strength are important considerations in choosing an implant material. The implant must have sufficient strength to withstand occlusal forces without permanent deformation and low modulus for optimum force transfer. Clinicians can choose the most appropriate dental implant material when they are knowledgeable about the properties of the materials. The surgical stainless steel alloys have a long history of use for orthopedic and implant devices. This alloy with titanium systems is used most often in a wrought and heat-treated metallurgic condition, which results in high strength and high ductility alloy.

Cobalt-Chromium-Molybdenum Based Alloys

The cobalt-based alloys are most often used in cast or cast and annealed metallurgic conditions.²² This permits the fabrication of implants as custom design, such as subperiosteal frames. The elemental composition of this alloy includes cobalt, chromium and molybdenum as the major elements. Cobalt provides continuous phase for basic properties. Chromium provides corrosion resistance through the oxide surface. Molybdenum provides strength and bulk corrosion resistance. All these elements are critical as their concentration emphasizes the importance of controlled casting and fabrication technologies. Also includes minor concentrations of nickel, manganese and carbon. Nickel has been identified as biocorrosive product and carbon must be precisely controlled to maintain mechanical properties, such as ductility. In general, the cast-cobalt alloys are least ductile of the alloy systems used for dental surgical implants and bending of finished implants should be avoided. Properly fabricated implants from these alloys have shown excellent biocompatibility profiles.

Iron-Chromium-Nickel Based Alloys

The surgical stainless steel alloys have a long history of use for orthopedic and implant devices.¹ This alloy with titanium systems is used most often in a wrought and heat-treated metallurgic condition, which results in high strength and high ductility alloy.

The ramus blade, ramus frame, stabilizer pins and some mucosal insert systems have been made from iron-based alloy. Among the implant alloys, this alloy is most subjected to pitting corrosion and care must be taken to use and retain the passiviated (oxide) surface condition, as this alloy contains nickel as a major element. Its use in allergic patients must be avoided. The iron-based alloys have galvanic potentials and corrosion resistance that could result in concerns about galvanic coupling and biocorrosion, if interconnected with titanium, cobalt, zirconium or carbon implant biomaterials. In some clinical conditions, more than one alloy may be present within the same arch of a patient. Long-term device retrievals have demonstrated that when used properly the alloy can function without significant *in vivo* breakdown. Clearly, the mechanical properties and cast characteristics of this alloy offer advantages with respect to clinical application.

Other Metals and Alloys

Many other metals and alloys have been used for dental implant device fabrication. Early spiral forms included titanium, platinum, iridium, gold, palladium and alloys of these metals. More recently, devices made from zirconium, hafnium and tungsten have been evaluated.²⁴ Some significant advantages of these reactive group of metals and their alloys have been reported. Gold, platinum and palladium are metals with relatively low strength values, which limit their use. These metals, especially gold, because of nobility and availability continue to be used as surgical implant materials.

CERAMICS

Ceramics are nonorganic, nonmetallic, nonpolymeric materials manufactured by compacting and sintering at elevated temperatures. They can be categorized according to tissue response as:

- Bioactive: Bioglass/Glass ceramic
- Bioresorbable: Calcium phosphate
- Bioinert: Alumina, zirconia and carbon.

Ceramics were introduced for surgical implant devices because of their inertness to biodegradation, high strength and physical characteristics, such as minimal thermal and electrical conductivity with a wide range of material specific elastic properties. Ceramics are chemically inert, care must be taken in handling and replacement due to its low ductility and inherent brittleness has resulted in its limitations.²⁵

Aluminum, Titanium and Zirconium Oxides

High ceramics from aluminum, titanium and zirconium oxides have been used for root form or endosteal plate form, and pin-type dental implants. The compressive, tensile and bending strengths exceed the strength of compact bone by 3 to 5 times. These properties combined with high moduli of elasticity and especially with fatigue and fracture strength have resulted in specialized design requirements for this class of biomaterials.

Advantages

- 1. The Al, Ti and zinc oxide ceramics have a clear, white cream or light gray color that is beneficial for application, such as anterior root form devices.
- 2. Minimal thermal and electric conductivity, biodegradation and reaction to bone, soft tissue and oral environment are also considered as beneficial when compared with other types of synthetic biomaterials.

3. Dental and orthopedic devices in laboratory animals and humans, ceramics have exhibited direct interface with bone similar to an osseointegrated condition with titanium.

Also, characterization of gingival attachment zones along with root form devices in laboratory animal model has demonstrated localized bonding.

Disadvantages

- 1. Exposure to steam sterilization results in a measurable decrease in strength for some ceramics.
- 2. Scratches or notches may introduce fracture initiation sites.
- 3. Chemical solutions may leave residues.
- 4. Hard and rough surfaces may readily abrade other materials thereby causing a residue in contact with the periapical tissues.
- 5. Dry heat sterilization within a clean and dry atmosphere is recommended for most ceramics.

Bioactive and Biodegradable Ceramics based on Calcium Phosphate

The calcium phosphate (CaPO₄) ceramics used in dental reconstructive surgery includes a wide range of implant types, and thereby a wide range of clinical applications.²⁶ Early investigations showed that nominal compositions were relatively similar to the mineral phase of bone $(Ca_5 [PO_4]_3)$ OH). The laboratory and clinical results of their particulate were promising and led to expansions for implant applications including larger implant shapes (such as rods, cones, blocks, H-bars) for structural support under relatively high-magnitude loading applications. Mixtures of particulate with collagen and subsequently with drugs and active organic compounds, such as bone morphogenetic protein (BMP) increased the range of possible applications. The coatings of metallic surfaces using flame or plasma spraying (or other techniques) increased rapidly for CaPO₄ ceramics. The coatings have been applied to a wide range of endosteal and subperiosteal dental implant designs with an overall intention of improving implant surface biocompatability profiles and implant longevity.

Advantages

- 1. Chemical compositions are highly pure and substances are similar to constituents of normal biologic tissue (calcium, phosphorous, oxygen and hydrogen).
- 2. Excellent biocompatibility profiles with variety of tissues, when used.
- 3. Minimal thermal and electrical conductivity and capabilities to provide a physical and chemical barrier to ion transport (e.g. metallic ions).
- 4. Moduli of elasticity more similar to bone than any other implant materials used for load-bearing implants.
- 5. Color similar to bone, dentin and enamel.

Disadvantages

- 1. Variations in chemical and structural characteristics for some currently available implant products.
- 2. Relatively low mechanical tensile and shear strength under condition of fatigue loading.
- 3. Relatively low attachment strengths for some coating to substrate interfaces.
- 4. Variable solubility depending on the product and clinical application.
- 5. Alterations of substrate chemical and structural properties related to some available coating technologies.

Bioactive Ceramic Properties

Tricalcium phosphate $[Ca_3(PO_4)_2]$ finds no place in this scheme, although it is frequently employed as a starting material in the synthesis of degradable ceramics. An explanation for this obscene was given that presence of water in CaPO₄ yields hydroxyapatite.

$$H_2O + 4Ca_3(PO_4) \rightarrow [Ca_{10}(PO_4)(OH)_2] + 2Ca^{++} + 2HPO_4$$

Apatite or more precisely hydroxyapatite is the main constituent of hard tissues, such as bone, dentin and enamel. Whenever a powder with Ca/P ratios in the order of 1.5 to 1.7 is sintered in atmosphere containing water at temperature up to 1200 to 1300°C, crystallographically the end product will be an apatite when comparing the elemental analysis.

Powder A: Commercially available is Merc W, Darmstadt, Germany, consists of very porous agglomerates with mean sizes of 1 to 2 mm. The specific surface area is determined by BET analysis is 59 m²/gm. X-ray analysis of powder shows broad peaks of the hydroxyapatite structure.

Powder B: It has been made according to the directions of Hayek (1963). Although, it is somewhat a tedious method due to gelatinous nature of the precipitate, it yields very finely divided powder with high surface area (80-90 m²/gm). Trace elements may influence biologic behavior.

Elemental Analysis

Contents	Powder A	Powder B
Calcium	37.5	37.2
Phosphorus	17.30	17.40
Hydrogen	0.50	0.50
Ca/P	2.167	2.138
Mol/Mol	1.68	1.66

Methods of Preparation

The powder is precompressed in a Perspex die by means of an upper and lower punch. To prevent the powder from sticking to the inner surface of the die, stearic acid in alcohol is applied. After the powder compact has been pushed out, it is placed into a rubber tube, brought under vacuum, isostatically compressed (100 MN/rn²) in oil containing press vessel. The samples compressed in this way have a density of 44% (green body) and heated at temperature, which increase at rate of 100°C/hr in wet O_2 atmosphere for 6 hours and cooled down slowly at 100°C/hr.

Preparation of Dense Apatite Crystals

Dudemans (1969) described a sintering technique called continuous hot pressing technique. In this method, heat and pressure are applied at same time, thus allowing densification to take place at a much lower temperature than in normal sintering process. First sintering occurs at 900°C, which is far below the decomposition temperature of hydroxyapatite. Continuous hot pressing is a fairly fast technique compared with conventional sintering. The die is heat punched at pressing rate of 25 mm/hr.

Forms, Microstructure and Mechanical Properties

Hydroxyapatite (HA) is a nonporous (< 5% porosity) with angular or spherically shaped particles, is an example of a crystalline high pure HA biomaterial. These particles have relatively high compressive strengths (up to 500 MPa) with tensile strengths in the range of 50 to 70 MPa.

Nonresorbable bioinert ceramics exhibits satisfactory load bearing capability limited to dense monocrystalline and polycrystalline aluminum, zirconium and titanium oxide ceramics. The coatings of CaPO₄ ceramics onto metallic (Co-and Ti-based) biomaterials have become a routine use for dental applications by plasma spraying, which has average thickness between 50 and 70 microns mixtures of crystalline and amorphous phases. Concerns continue to exist the fatigue strengths of the CaPO₄ coatings to substrate interfaces under tensile and shear loading conditions. This has caused some clinicians and manufactures to introduce geometric designs in which the coatings are applied to shapes that minimize implant interface shear or tensile loading conditions.

Density, Conductivity and Solubility

Bioactive ceramics are especially interesting for implant dentistry because the inorganic portion of the recipient bone is more likely to grow next to chemically similar material. Under the bioactive categorization includes calcium phosphate materials, such as TCP (tricalcium phosphate), HA, calcium carbonate (cards) and calcium sulfate-typecompounds and ceramics.

Dissolution characteristics of bioactive ceramics have been determined for both particulate and coatings. In general, solubility is greater for TCP than for HA. Each increase relative to increase in surface area per unit volume (porosity) and $CaPO_4$ ceramic solubility profiles depend on the environment. Tofe et al studied the product impacts on the resorption rate. Greater the porosity more rapid is the resorption of graft material.

The crystallinity of HA also affects the resorption rate of the material. The highly crystalline structure is more resistant to alteration and resorption. An amorphous product has a chemical structure that is less organized with regard to atomic structure. The hard and soft tissues of the body are more able to degrade the components and resorb the amorphous forms of grafting materials. Thus, the crystalline forms of HA are found to be very stable over the long-term under normal conditions, whereas the amorphous structures are more likely to exhibit resorption and susceptibility to enzyme or cell-mediated breakdown. The purity of the HA bone substitutes may also affect the resorption rate. The resorption of the bone substitute may be cell- or solutionmediated. The cell-mediated resorption requires processes associated with living cells to resorb the material, similar to the modeling/remodeling process of the living bone.

A solution permits the dissolution of the materials by a chemical process. Impurities or other compounds in bioactive ceramics, such as calcium carbonate, permit more rapid solution mediated resorption, which increases the porosity of the bone substitutes.

The CaPO₄ coatings are nonconductors of heat and electricity. This can provide a relative benefit for coated dental implants, where mixtures of conductive materials may be included in the overall prosthetic reconstruction.

Hydroxyapatite-Coated Metals

The achievement of improved metallic bone implant devices by simply coating them with HA proved to be remarkably easy, both in concept and execution.²⁷ From the point of view of execution, standard methods for putting ceramic coatings on implants are principally plasma or flame spray technique has been around for decades. HA plasma coating process involves first roughening the metal to be coated in order to increase the surface area available for mechanical bonding with HA coating. Then a stream of HA powder is blown through a very high temperature flame that partially melts and ionizes the powder, which emerges from the flame, hits the metallic surface to be coated and condenses to form a ceramic coating that is partially glossy and partially crystalline in nature. These coatings are built up in thin layers using robotic techniques, until the final thickness (usually 40-100 μ) is achieved. The major shortcoming of HA ceramics is their lack of mechanical strength. The major strength of HA is a chemical composition, which fools living bone tissue behaving as if the HA implant were natural autogenous bone.

Hydroxyapatite-Tricalcium Phosphate Bioceramics

The two calcium phosphate systems that have been most investigated as bone implant material are HA and tricalcium phosphate. Based on numerous *in vitro* and *in vivo* experiments,²⁸ it was apparent that dense or porous HA ceramics could be considered to be long-term or permanent bone implant materials, whereas porous TCP ceramic could potentially serve as bioresorbable. Although TCP implant materials were more or less comparable to HA material with regard to biocompatability and bone bonding, achieving predictable and reproducible bioresorption rates with adequate mechanical properties proved to be difficult with TCP ceramics. TCP system became eclipsed by a succession of commercially introduced HA containing implantable products.

HA, commonly called tribasic calcium phosphates, is a geologic mineral that closely resembles the natural vertebrate bone tissue. These materials must not be confused with tricalcium phosphate (TCP), which is chemically similar to HA but it is not a natural bone material.

Types of Ceramic Coatings

The ceramic coating available includes the bioactive type, such as the calcium phosphates and inert ceramics, such as aluminum oxide and zirconium oxide. The bioactive ceramics include the bioglasses, have been documented to produce a calcium phosphate layer on the unmodified surface when used *in vivo* or in a simulated physiological solution. Primary importance as far as response is concerned is the amount of calcium and phosphate ions released per given amount of time. The presence of calcium and phosphorous ions in the area around the implant often resulted in enhanced bone apposition as compared with the more ceramic and metallic surfaces. It is important to realize that all coating processes are likely to alter the composition of the starting material to some degree and have the potential for introducing impurities into the coating.

Plasma Spraying

It is the most common coating method for dental implants because almost all the commercial HA coatings are produced by this technique.²⁹ This method involves the use of a carrier gas, which ionizes (thus forming a plasma) and superheats the particles of the starting material (generally HA), undergoes partial melting as they are propelled toward the substrates to be coated. Coatings around 50 microns are typically produced on a roughened titanium or alloy surface for a HA (plasma) sprayed endosseous implant. The most stable of the plasma sprayed calcium phosphate coatings is fluorapatite (FA), which is capable of retaining in large part both its fluorine constituent and high crystallinity during the high temperature plasma spray process. This process has a crystallinity of around 60 to 70%, but higher content can be obtained if the coated implant is heat-treated at a suitable temperature after the deposition process. One study showed that a low crystallinity (46% HA) plasma-sprayed implant exhibited about three times the dissolution of Ca ions as a higher crystallinity (75% HA) material.

Advantages

- 1. It is relatively inexpensive
- 2. The mechanical properties of the metallic substrate are not compromised during the coating process.

Limitations

- 1. Forms mechanical bonding only with the metallic implant surface
- 2. The main source of contamination appears to be copper from the nozzle of the sprayers

Vacuum Deposition Techniques

There are several methods of placing thin coatings of ceramics on metals, as done routinely in the electronics and other industries. These involves bombarding a target in vacuum chamber resulting in sputtered or ablated atoms or particles moving through the chamber to coat on properly positioned substrates. These techniques include ion beam sputtering, radio frequency sputtering and pulsed laser deposition. All are relatively expensive and capable of depositing coatings in the order of a few micrometers.

Advantages: High quality coatings with good bonding to either smooth or rough titanium surfaces, but usually require a heat treatment in a controlled atmosphere to attain high crystallinity.

Limitations

- 1. The efficacy of these very thin coatings is unknown
- 2. There is some concern that the coating may resorb in the body before causing the desired effect.

Sol-gel and Dip Coating Methods

Studies on the use of sol-gel technology for coating dental implants have recently been initiated. This method had been used for depositing other types of thin coatings, such as superconducting thin films for electronic devices. In this technique, precursors of the final product are placed in solution, and the metal implant to be coated is dipped into the solution, withdrawn at the prescribed rate, and then heated to create a more dense coating.

Technique: The coating is fired at 800 to 900°C to melt the carrier glass to achieve bonding to the metallic substrate. This process is repeated until a relatively thick coating (e.g. 100 microns) consisting of HA/glass mixture can be obtained.

Advantages

- 1. Small crystalline size and high strength
- 2. Potential for applying a uniform coating to porous substrates.

Hot Isostatic Pressing

Hot isostatic pressing (HIP) is used to develop the highest density and strength possible in crystalline ceramic materials.

In this technique, both heat and pressure are used to enhance ceramic density (such as alumina or HA) into a solid ceramic of high strength. HA powder is applied to the implant surface, an inert foil is placed over the powder to facilitate uniform densification, both heat and pressure are applied.

Disadvantages

- 1. Expensive
- 2. The necessity of removing the inert foil or other encapsulating material
- 3. The potential for contamination.

Electrolytic Process

Electrophoresis and electrolytic deposition are two processes that deposit HA or suitable bioceramic particles out of a bath of proper chemistry.

The advantages are that the porous surface materials can be uniformly coated, and the original composition of the ceramic (e.g. HA) can be maintained in most cases.

In the present state of development, none of the coating techniques discussed produce HA coatings with both high crystallinity and high bond strength. Heat treatment may be used to increase crystallinity. However, they are not widely used because of the added expense and increased possibility of contamination of the coatings. Manufacturers can often obtain the desired crystallinity (e.g. higher than 80%) during the plasma spray coating operation without the need for additional heat treatment.

Carbon and Carbon Silicon Compounds

Carbon compounds are often classified as ceramics because of their chemical inertness and absence of ductility.

Uses

- 1. Extensive applications for cardiovascular devices
- 2. Excellent biocompatibility profiles and moduli of elasticity close to that of bone have resulted in clinical trails of these compounds in dental and orthopedic prostheses.

Advantages

- 1. Tissue attachment
- 2. Can be used in the regions that serve as barrier to elemental transfer of heat and electrical current flow
- 3. Control of color and provide opportunities for the attachment of active biomolecule or synthetic compounds.

Limitations

- 1. Mechanical strength properties are relatively poor.
- 2. Biodegradation that could adversely influence tissue stability.
- 3. Time dependent changes in physical characteristics.
- 4. Minimal resistance to scratching or scraping procedures associated with oral hygiene.

Bioactive Glass Ceramics

Bioglass (US: Biomaterials) is composed of calcium salts and phosphates in similar proportions found in bone and teeth.³⁰ This graft is amorphous material, hence its developers believed that degradation of the material by tissue fluids and subsequent loss of the crystal would cause the material to lose its integrity.The graft has two properties:

- 1. Relative quick rate of reaction with host cells
- 2. Ability to bond with collagen found in connective tissue. It has been reported that the high degree of bioactivity induces osteogenesis. Since the bioactivity index is high, reaction develops within minutes of implantation.

Tissue Response

 $CaPO_4$ ceramics, particularly HA, have been used in monolithic form as augmentation material for alveolar ridges and coatings on metal devices for endosseous implantation. The implant surface responds to the local pH changes by releasing sodium ions in exchange for phosphorous ion. Osteoblasts proliferate at the surface and collagen fibrils become incorporated into the calcium phosphate rich layer. The body's typical response to these implanted ceramics are:

- No local or systemic toxicity
- No inflammatory or foreign body response
- Functional integration with bone
- No alteration to natural mineralization process
- Chemical bonding to bone via natural bone cementing mechanism.

The natural bone cementing substance is amorphous in structure, heavily mineralized and rich in polysaccharides. Because the bond area contains the natural bone cement substance, it is responsible for the bond between bone and the calcium phosphate ceramic is strong.

Current Status and Developing Trends

The CaPO₄ ceramics have proved to be one of the more successful high technology based biomaterials that has evolved within the biomaterials in the past two decades. Their advantageous properties strongly support the expanding clinical applications and the enhancement of the biocompatibility profiles for surgical implant uses.

Within the overall theme for new generation biomaterials to be chemically (bonding to tissue) and mechanically (nonuniform, multidirectional properties) anisotropy, the $CaPO_4$ ceramics could be the biomaterial surfaces of choice for many device applications.

Ceramic forms of calcium phosphate, particularly HA, had been investigated extensively and used for hard tissue implant applications. HA ceramic still remains the most biocompatable bone material known and posses the added feature of becoming strongly bonded to living bone through natural appearance bonding mechanism. A variety of new or improved bone and tooth implant products have been developed using HA ceramics, thus this system had lead to overall improvement in dental hard tissue repair and replacement.

POLYMERS AND COMPOSITES AS IMPLANT MATERIALS

The use of synthetic polymers and composites continues to expand for biomaterial applications. Fiber-reinforced polymers offer advantages that they can be designed to match tissue properties, can be coated for attachment to tissues and can be fabricated at relatively low cost. Expanded future applications for dental implant systems include IMZ (Interpure Inc) and Flexiroot (Interdent Corp). Systems are anticipated as interest continues in combination of synthetic and biologic composites.

Biomedical Polymers

The more inert polymeric biomaterials include polytetrafluroethylene (PTFE), polyethyleneterephthalate (PET), polymethylmethacrylate (PMMA), ultra high molecular weight polyethylene (UHMW-PE), polypropylene (PP), polysulfone (PSF) and polydimethyl siloxane (PDS) or silicone rubber (SR).

Properties

In general, the polymers have lower strengths and elastic moduli, and higher elongation to fracture compared with other class of biomaterials. They are thermal and electrical insulators, and when constituted as a high molecular weight system without plasticizers, they are relatively resistant to biodegradation compared with bone; most polymers have lower elastic moduli with magnitudes closer to soft tissues. Polymers have been fabricated in porous and solid forms for tissue attachment, replacement and augmentation as coatings for force transfer to soft and hard tissue regions. Cold flow characteristics, creep and fatigue strength are relatively low for some class of polymers (e.g. SR and PMMA) that had resulted in some limitations.

Most uses have been for internal force distribution connectors intended to better stimulate biomechanical conditions for normal tooth functions. The indications for PTFE have grown exponentially for guided tissue regeneration techniques. However, PTFE has a low resistance to contact abrasion and wear phenomenon.

Polymers and Composites

Combinations of polymers and other categories of synthetic biomaterials continue to be introduced. Several of the inert polymers have been combined with particulate or fibers of cotton, aluminum oxide, and hydroxyapatite and glass ceramics. Some are porous whereas others are constituted as solid composite structural forms. In some cases, biodegradable polymers, such as polyvinyl alcohol (PVA), polylactides or glycosides, cyanoacrylates or other hydrated forms have been combined with biodegradable $CaPO_4$ particulate of fibers. They are intended as structured scaffolds, plates, screws or other such applications. Biodegradation of the entire system after tissues have adequately reformed, and remodeling has allowed the development of significantly advantageous procedures, such as bone augmentation and peri-implant defect repairs.

Disadvantages

- 1. In general, polymers and composites of polymers are especially sensitive to sterilization and handling techniques. If intended for implant use, most cannot be sterilized by steam or ethylene oxide.
- 2. Most polymeric biomaterials have electrostatic surface properties and tend to gather dust or other particulate if exposed to semiclean oral environments.
- 3. Because many can be shaped by cutting or autopolymerizing *in vivo* (PMMA), extreme care must be taken to maintain quality surface conditions of the implant.
- 4. Porous polymers can be deformed elastically, which can close open regions intended for tissue ingrowth.
- 5. Also, cleaning the contaminated porous polymers is not possible without a laboratory environment.

Implications

Long-term experience, excellent biocompatibility profiles, ability to control properties through composite structures and properties that can alter to suit the clinical application make polymers and composites excellent candidates for biomaterial applications, as the constant expansion of the applications of this class of biomaterials can verify.

FUTURE AREAS OF APPLICATION³¹

Synthetic substance for tissue replacements have evolved from selected industrial grade materials, such as metals, ceramics, polymers and composites. This situation offers opportunities for improved control of basic properties. The simultaneous evaluation of the biomechanical sciences also provides optimization of design and material concepts for surgical implants. Combinations provided are compositions with bioactive surfaces, the addition of active biomolecules of tissue inductive substances and a stable transgingival attachment mechanism that could improve implant device systems. Devices that function through bone or soft tissue interfaces along the free transfer regions could be the systems of choice depending on the clinical situation.

The trend for conservative treatment of oral diseases will continue. Thus, it can be anticipated that dental implants will frequently be a first treatment option. Implants have rapidly moved into the mainstream of dental practice in the last 10 years with phenomenal growth based on rapidly expanding technology with increasing public interest. Implants have been used to support dental prostheses for many decades and they have always enjoyed a favorable reputation.

CONCLUSIONS

Dental implantology is an exciting treatment concept that includes series of surgical, prosthetic and periodontal restorative skills. In the 1960s and early 1970s, dental implantology was considered somewhat experimental and basically restricted to early workers. The phenomenal interest, clinical application, improvement in dental materials and biomechanical understanding by dental scientists in this field led to carefully conduct controlled and monitored clinical trials. Implantology has become an exciting and dynamic force within dentistry during the recent years, from a less than well-accepted treatment option, it has mushroomed into the current hottest issue in dentistry. Implantology provides many new and exciting ways to help dental patients to achieve function and social well-being, and provide a certain amount of personal and professional satisfaction to the dentist. Dental Implantology will become a highly acceptable and predictable treatment modality for the restoration of the human dental and oral apparatus. Implants are now being targeted in predoctoral and postdoctoral training program nationally and internationally. Though, we have come a long way, and may be we haven't seen anything yet.

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