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REVIEW ARTICLE

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Bioactive coating as a surface modification technique for biocompatible metallic implants: a review

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ABSTRACT
Most high load-bearing implants are metallic alloys which contain toxic chemical components that might be released due to the corrosive environment of body fluids and load-bearing activity. Surface modification techniques do not guarantee biocompatibility. Hence, the bioactive surface of implants can be modified by coating the surface with a suitable material that addresses the needs of the patient. The choice and application process of the coatings should be determined based on the workability of the material and its physiochemical properties, such as the procedures involved and performance in avoiding removal of any desirable material properties that are helpful in the tissue regeneration process. Tailor-made coating materials prove very promising, as they might improve permanent implantations, make them more affordable and reduce the need for surgical revisions. The scope of the featured properties, such as addition of accelerated tissue regeneration, antibacterial properties and controlled release and removal of debris from the biological system to the metal implants makes coatings an ideal choice for surface modification of implants. This report reviews several options available for forming a biologically active layer over metallic surfaces that will interact with and produce desirable effects on host tissues.

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Biocomposite; apatite; implant; coating; osteointegration; corrosion

1. Introduction

The use of surgical implants is a rapidly expanding node of the healthcare industry. The materials should not only be deployed satisfactorily but should also be able to withstand the extreme environments created by locomotion and body fluids without any associated side effects. In some cases, implants have been reported to grow bacterial colonies which not only pose serious issues but which also act as another factor leading to implant failure and surgical revisions brought about by eventual detachment of the implant as a direct result of colonization. Structurally and morphologically tailored materials have proved to be of great interest in countering such issues along with the biocompatibility of the materials with surrounding tissues. The past few decades have seen a steep rise in the development of implants, with research now targeting multifunctional tailor-made implants. Apart from biological analogue implants such as those based on β-TCP and HAP, there is a class of metallic implants which despite their offering of proper mechanical properties, pose serious issues related to corrosion that is manifested in organ and tissue anomalies in response to increased ion concentrations. The most commonly used implants include stainless-steel, cobalt-chromium alloys and titanium-based implants [1]. Despite their low rates of failure, these represent a considerable number of surgical revisions which researchers have attempted to reduce by surface modification techniques such as anodization, electropolishing and ion implantation. The techniques aimed at corrosion have failed to deal with microbial invasion and biocompatibility issues which have triggered increasing interest in coating of such implants to achieve better biocompatibility and withstand adverse environments thereby regulating the implants performance.

Biocomposites made of ceramics and polymers, despite their better performance toward bioactivity, can never match the strength and stability of metallic implants. Recent decades have seen a rapid increase in research toward the application of bioceramics and other apatite-based coatings to cover metallic implants. A survey of the literature also supports the successful application of ceramic-based coatings over metallic implants with desirable results. Such coatings may also deploy ceramic/ceramic as well as ceramic/polymer composites with the coating procedure depending on the constituents of the coating and its physiochemical properties.

2. Metallic implants

Metals play an important role in the human body as implants. Metallic alloys are most commonly used in all bone joint replacements and dental implants. Most

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metallic implants find application in orthopedic surgery due to such advantages as their higher tensile strength and fatigue resistance as compared to ceramics and polymers. Several types of metals have been used in biomedical implants, including stainless steel, Co-Cr alloys and titanium and its alloy [2–5]. The applications and mechanical properties of the metallic implants are given in Table 1.

2.1. Stainless steel

316L SS and 316L VM are the most widely used alloys for such biomedical applications as implants. 316L SS contains iron, chromium, nickel and molybdenum ions. Chromium protects implants from corrosion and also forms an oxide layer on the surface of the metals by a process of passivation. 316L contains low carbon content, which prevents corrosion in the human body. Even though stainless steel is corrosion resistant, it may corrode in the presence of chlorine ions. About 90% of 316L stainless-steel implants have shown pitting and crevice corrosion and surface coating with ceramic materials has to prevent corrosion of 316L stainless steel. 316L VM is another type of stainless steel with corrosion resistance properties that have been used for biomedical applications. Okazaki et al. have studied the use of 20 metallic 316L SS to replace of charnels hip arthroplasty in the human body [6]. After 13 years of implantation, the release of metal ions at increased concentrations was observed in the body fluid. These metal ions (corrosion products) lead systemically to local inflammation and eventual loosening of artificial joint implants. The failure of stainless steel was reported, and the problem such as crevice corrosion, pitting, and initiation of cracks, intergranular corrosion and surface cracking has been observed in the thighs of the patients [7]. In addition, Sivakumar et al, reported about crevice corrosion and its important role in damage to the implants [8]. Stainless steel has a Young's modulus of 200 Gpa, which is greater than that of bone and will lead to eventual detachment due to differences in mechanical properties and behavior. Thus, stainless-steel is appropriate for use only in short-term applications such as nonpermanent fracture fixation devices because of its low cost, easy manufacture and applicability [9].

2.2. Cobalt-chromium alloy

Cobalt-chromium alloys consist of 58–70% cobalt, 26–30% chromium and a small quantity of other metals. Chromium alloys form a passivation oxide (Cr_2O_2) layer in its alpha phase. Hence, it is highly resistant to corrosion, even in a chloride environment. This passivation makes Co-Cr viable choice for long-term application than stainless steel. The mechanical properties of Co-Cr such as high strength and desirable fatigue and wear resistance make it applicable in total joint replacement in the hips or knees, etc., but the replacements are not ductile in nature with a minimum elongation of 8%. Co-Cr-Mo (6% molybdenum) is another widely used alloy for medical implants especially in dentistry for long-term applications and in femoral head of joint prosthesis. The elastic modulus of Co-Cr (220–230 Gpa) is higher than that of bone (30 Gpa). Bio-corrosion causes adverse effects on implants by releasing metal ions, which is a major disadvantage of cobalt-based alloys. Ni and Co ions present in Co-Ni-Cr-Mo alloys can lead to allergic reactions. Ni specifically, carcinogenic and the metal ions released may induce adverse effects [10]. The corrosion product of Co-Cr-Mo is more toxic than that of stainless steel.

2.3. Titanium and its alloys

Since 1970, titanium and its alloy have been used extensively as implants that have distinguished properties such as high mechanical strength, corrosion resistance, low density, and biocompatibility. It forms a stable oxide layer on the surface that passivates and protects from corrosion [11]. Titanium is a pure metal, and it can be alloyed with vanadium (V) and aluminum (Al). According to the American society of testing materials (ASTM), commercially available pure titanium (Cp Ti) comes in

Table 1. Applications of biomaterials and their mechanical properties.

Biomaterials	Applications	Mechanical properties: Young's modulus(Gpa)	Mechanical properties: Tensile strength	Mechanical properties: Hardness(H_v)
Stainless steel	Join replacements (hip and knee), bone plate for fracture fixations, dental implants, heart valve, spinal, hip nail, shoulder prosthesis.	200	586–1351	190
Titanium and its alloys	Cochlear replacements, bone and joint replacements, dental implants, suture for orthodontic implant, artificial heart valves, and pacemakers.	110	760	-
Cobalt chromium	Bone plate, screws, dental implant (root) pacer and suture, orthopedic implants, total bone and joint replacements (hip and knee) mini plates.	220–230	655–1896	450
Alumina	Artificial total joint replacement, acetabula, femoral components, vertebrae spacer and extensor, orthodontic anchors and dental implants	380	350	2000–3000
Zirconia	Replacement of hip, knee, teeth tendons, ligaments, repairs for periodontal disease, bone fillers.	150–200	200–500	1000–3000
Calcium phosphate	Skin treatments, dental fillings, jawbone reconstructions, coatings on implants in orthopedics, facial surgery, and throat repair dental implants.	40–117	69–193	350

four grades (I-IV), which contain a small quantity of oxygen, nitrogen, hydrogen, iron, and carbon. Further, a report by Davidson and Georgette has revealed that about 2.2 million pounds of titanium implants have been widely used in patients and their excellent corrosion-resistance properties make them a preferred choice for biomedical applications [12,13]. The high elastic modulus of the implants can lead to stress-shielding effects and result in failure of the implants and Ti implant have been developed with an elastic modulus of 110Gpa lower than those of stainless steel (210Gpa) and Co-Cr alloys (240Gpa). Titanium-based alloys have applications in joint replacement, bone fixation, screws, plates, dental implants, heart implants, pacemakers, artificial heart valves, and stents. Commercially pure titanium is allotropic in nature with a hexagonal α-phase (HCP). At 88.2ºC, it exists in the hexagonal α-phase (HCP) and at temperature above 88.2ºC; it forms the body-centered cubic β-phase.

To improve the strength of pure titanium, metals such as Al, Mo, V, Nb, Ta, Mn, Fe, Cr, CO, Ni, and Cu are incorporated into it [14–16]. Different types of titanium alloys that have been developed for bone applications are Ti-Al-4V, Ti-Nb-7A-Zr, Ti-Ni-Ta, Ti-15MO-5Zr-3A, Ni-Ti, and Ti-Sn-Nb. Titanium with such alloys as 6% aluminum and 4% vanadium is designated as Ti-6Al-4V which has a lower iron and oxygen content and are the most efficient aluminum-Ti alloys. Steinmann (1980) has reported that vanadium and aluminum are toxic and can cause peripheral neuropathy and osteomalacia, and that it can cytotoxic and cause severe tissue damage [17]. Matsumoto et al. developed Ti-26Nb-13Na-4.6Zr and Ti-Nb-Sn and they found that the metals have a lower Young's modulus and higher yield strength than stainless-steel, Co-Cr alloys [18,19]. A comparative study of the corrosion-resistance behavior of CP-titanium and Ti-6Al-4V with other titanium-based alloys carried out in hank solution found that the corrosion rates are in the following order:

$$\mathbf{CP-Ti} > \mathbf{Ti-6Al-4V} > \mathbf{Ti-15V-3Cr-3Al-3Sn} > \mathbf{Ti-20Nb-20Zr} > \mathbf{gunmetal} > \mathbf{Ti-13Nb-13Zr}.$$

Nitrogen ion implantation and heat treatment enhance the fatigue resistance of Ti-6Al-4V by the formation of a vanadium-oxide passivation layer. The addition of Nb to the Ti-6Al-4V alloy results in the formation of Nb-rich peroxide, which is more resistive to corrosion and stable in the human body [20]. Corrosion resistance depends on the thickness of the oxide layer and the nature of titanium. It was found that Ni-Ti causes such adverse effects as severe cell death. Furthermore, titanium implants can be used for lifetime applications more reliable than stainless steel and Co-Cr alloys.

3. Implant corrosion

Metallic materials are strongly preferred for implants due to their high strength, ductility, and toughness; however, implant corrosion stemming from leaching of metallic ions into the surrounding tissues is a major drawback [21,22]. A better understanding of basic electrochemical reactions is mandatory in every stage of the implantation procedure, from design to production of the finished product.

Upon implantation, the existence of a passive film on the surface of metallic implants should control the corrosion process by the release of low-level corrosion products for successful implantation. However, the complex physiology of body fluids, especially dissolved gases, proteins, and various ions, as well as temperature effects an oxygenated saline solution makes the environment aggressive and can lead to implant corrosion. The leaching out of metal ions is found to be highly toxic to the cells. Elements such as Pb (lead), Hg (mercury), As (arsenic) and Be (beryllium) are known to be toxic, and their use is avoided in clinical applications. Some other metals like Fe (iron), Al (Aluminum), Cr (Chromium), V (Vanadium) and Co (cobalt) have been found to induce proliferative effects in the tissue regeneration process. Some significant tests of lymphocyte blastization have arranged the toxicity level of metals as follows:

$$\mathbf{Ti} > \mathbf{stainless\ steel} > \mathbf{Cr} > \mathbf{Ni} > \mathbf{Mo} > \mathbf{Co} > \mathbf{Cu}$$

Compared with other metallic implants, titanium produces passive layers such as TiO_2, which is nontoxic and inhibits autocatalysis reactions between titanium and the surrounding body fluids. These metal ions may lead to denaturing of the proteins and even to eliciting an immunological response followed by damage due to deposition in the organs. The accumulated ions in an organ may affect the normal function of metabolism and cause renal and cardiac issues. In addition, the mechanical load under normal living conditions also has a chance of increasing the rate of corrosion due to mechanical effects in action [23].

4. Failure of implants

After implantation, the performance of an implant falling below a specific acceptable level is a major issue that affects its intended therapeutic time and can even lead to surgical revisions. The biocompatibility, functionality, and retention of the implant material should be positively encouraged and focused on the interaction between the material and the host system [24]. Various factors, such as particulate matter and debris from ions (caused by corrosion/wear), fibrous encapsulation (caused by insufficient bone integration), inflammation, low fracture toughness, low fatigue strength, variations in the modulus of elasticity of the implant material and the surrounding bone (stress shielding) and infection can lead to failure of an implant, as illustrated in Figure 1.

This unstable fixation of implants can overcome by stable, rapid bone formation in the deficient bone site that makes for firm fixation of an implant to the adjacent bone. To accomplish the requisite surface properties of the implant material, an appropriate surface modification procedure is necessary to enhance its biomedical applications. Hence, the material comprising an implant should be well tolerated by the biological system. The implant causes the development of a fibrous collagen sheath of low cellularity, which encapsulates and separates the implant from normal tissue. If the thickness of the sheath around the implant is very thin, the tolerability by the host system is easy and fewer corrosion products are formed [25,26].

4.1. Mechanism of implant failure

Uncoated metal implants have a chance of causing implant loosening or rejection coupled with bacterial colonization. Even when coated with a bioactive material, the rate of dissolution of a coating may decrease the lifetime of an implant. Rapidly dissolving HAP coatings are resorbed by osteoclasts. The resorbed coatings are integrated into the normal bone remodeling process and replaced with new bone by the osteoblasts. The dissolution rate of HAP coatings is significant because a rapidly dissolving coating can lead to bone growth. However, rapid dissolution of the coating may also lead to loss of fixation, implant loosening and the production of particle debris [27].

The second mechanism of implant failure with surface coatings is attributed to third-body wear, which results in osteolysis. Osteolysis is degradation of the bone caused by osteoclasts, or bone-resorbing cells. Mechanical stress placed on a hip implant by the patient is believed to be the source of third-body wear.

5. Surface modification techniques

In selection of a suitable surface modification technique with nontoxicity for specific biomedical applications, corrosion resistance, modulus of elasticity, fatigue strength and controlled degradability have been recognized as basic properties. The rationale behind surface modification of an implant is that the surface of a material determines the response of the biological environment to implanted materials. Surface modification of implants is broadly classified into two approaches: accelerated bone healing and enhanced bone bonding of an implant.

In the enhanced bone-bonding approach, the surface topography of an implant material is modified using a suitable approach that enables the modified surface to increase the mechanical interlocking of the bone with the implanted material. The modified surface automatically increases the surface area and surface energy of the material, which leads to enhanced matrix protein absorption, cell adhesion and proliferation, and finally, to better osteointegration of the implant with the bone. Mechanical processing is simple physical treatment and shaping of a material surface by cutting, blasting, grinding and polishing to produce an improved surface topography and roughness, remove contaminated materials and reinforce its bonding strength by way of increased adhesion.

In accelerated bone healing, inorganic or composite bone materials are incorporated into the bone's surface to enhance the bone-forming capability of the cells and cause biochemical interlocking of the implant with the adjacent bone. Incorporation of organic molecules (biochemical) such as proteins and peptides into the surface of the implant is also an accelerated bone-healing method.

5.1. Types of coating

Various coating techniques have been employed. Mechanical methods such as electrophoretic coating, plasma spray, laser deposition, biomimetic deposition

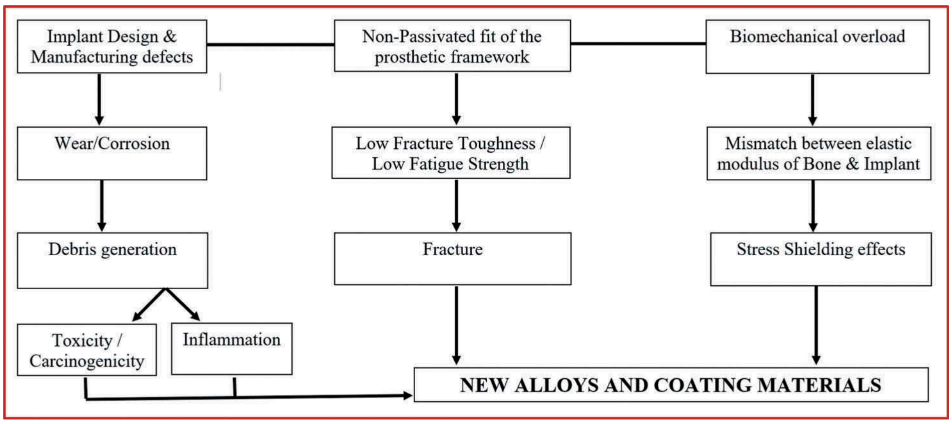

Figure 1. Various factors responsible for implant failure.

and wet methods such as sol-gel-based spin- and -dip or spray-coating deposition have been used most often for coating implants. The advantage and disadvantages of the various types of coating are listed in Table 2.

- The Thermal spray method developing in many directions. Probably the most exciting developments in coatings revolve around new applications. Examples include coatings that are applied to new forms of energy generation such as electrolysis, self-cleaning of surfaces by photocatalysis, biomaterials, electronic-based functionalities, and many others.
- Magnetron sputtering has been used in the process of deposition of industrially important wear-resistant coatings, low-friction coatings, corrosion-resistant coatings, and decorative coatings.
- The pulsed-laser deposition (PLD) technique is a physical phenomenon employing a laser to ablate a target material and condense it on the surface of a substrate.
- Ion-beam deposition is used to grow ultra-pure epitaxial thin films at low temperature and produce unique film properties not obtained with conventional deposition methods.

Two types of wet-chemical methods, the biomimetic and sol-gel methods have been employed in biomedical applications. These techniques involving mild chemical preparation conditions form a three-dimensional coating on the substrate, which cannot be done using physical techniques. The biomimetic method is a simple technique involving immersion of a metal substrate into an SBF solution to produce a coating on the surface.

- The sol-gel technique, on the other hand, is a simple-wet chemical route to biomaterial synthesis that requires no high pH value and no high sintering temperatures. Sol-gel coating is a colloidal suspension of solid particles (1–500 nm) in a liquid solution, or "sol". A sol can be deposited on a substrate with a spraying, dip-coating, spin-coating or doctor-blading technique as illustrated in Figure 2. The gel on the substrate is calcined or dried to form a thin layer on the surface. In this technique, calcium phosphate layers are prepared by inserting a metal sample in calcium and phosphorus gel at low temperature. As the layer formed is porous and less dense, the coated layer is calcined at 400–600ºC depending on the material. A second layer of coating can be applied to improve its bonding strength by forming a multilayer deposition of the material over the implant [28].
- The Electrophoretic deposition (EPD) technique involves the migration of charged particles in the electrolytic solution and has been extensively reviewed. The ceramic particles attain a charge from an electric field in an aqueous or non-aqueous medium. Deposition of thin films on an implantable material's surface characteristically increases the wear and corrosion resistance of titanium implants, when the protection offered by the original surface oxide layer is insufficient. A schematic diagram of the electrophoretic deposition (cathodic, anodic) forming process is illustrated in Figure 3. The suspension in an EPD set up consists of homogeneously dispersed powder particles in an aqueous or non-aqueous medium along with the respective anode and cathode electrodes. Both cathodic and anodic depositions are possible depending on the particles, positive or negative charge. If the suspended particles are positively charged, they will be deposited in the cathodic compartment, whereas negatively charged particles

Table 2. Advantages and disadvantages of various coatings.

Types of coating	Thickness	Advantages	Disadvantages
Thermal spraying	30 to 200 μm	High deposition rates. Low cost.	High temperatures induce decomposition. Rapid cooling produces amorphous coatings
Magnetron sputtering	0.5 to 3 μm	Uniform coating thickness. High adhesion. Dense, pore-free coating. Ability to coat on heat- sensitive substrates.	Expensive. Low deposition rates produce amorphous coatings.
Pulsed laser deposition	0.05 to 5 μm	Coating with crystalline and amorphous phases. Dense and porous coating.	Expensive. High temperature prevents from simultaneous incorporation of biological agents.
Ion beam deposition	0.05 to 1 μm	High adhesive strength. Uniform coating thickness.	Expensive. Produce amorphous coatings.
Sol–gel technique	< 1μm	High adhesive strength.	Inexpensive. Low processing temperatures. Thin coatings. Required controlled atmosphere. High cost of precursors.
Electrophoretic deposition (EPD)	0.1 to 2.0 mm	Uniform coating thickness. Rapid deposition. Coat complex substrate.	Difficult to produce crack- free coatings. Required high sintering temperatures

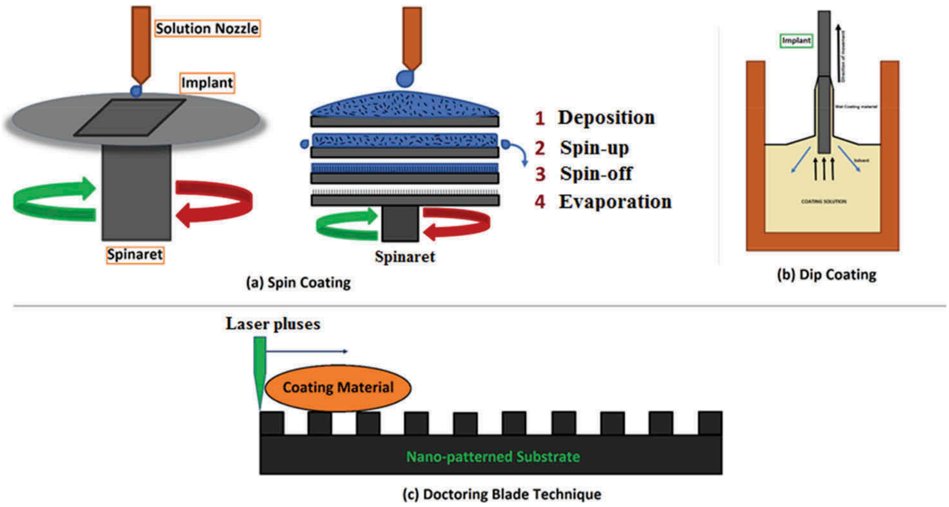

Figure 2. Types of sol-gel deposition on implant substrates (wet-coating techniques).

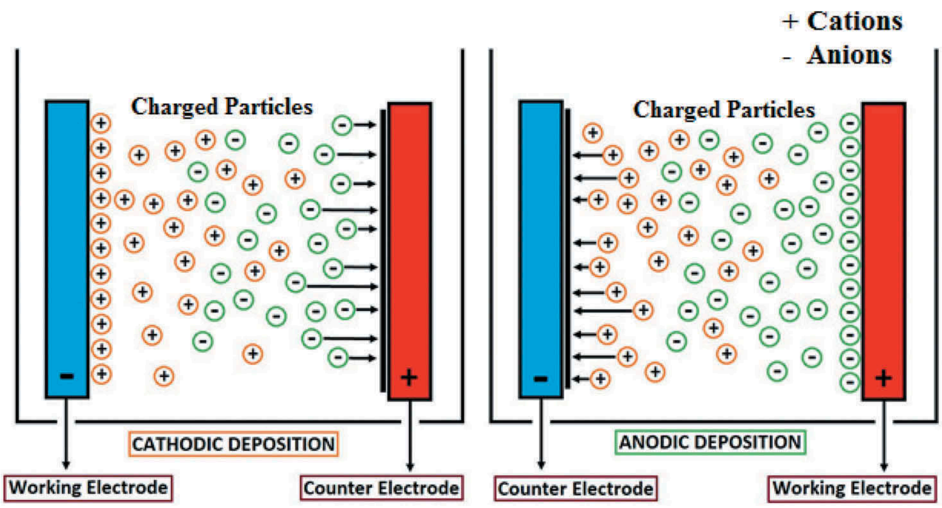

Figure 3. Schematic diagrams of electrophoretic deposition (EPD) on metal substrates (working electrodes).

move toward the anode. Besra and Liu further reviewed the nature of the suspension and processing parameters affecting electrophoretic deposition. Suspension parameters such as the particle size, dielectric constant, conductivity and zeta potential determine the quality of the suspension, while physical parameters such as the voltage, deposition time and conductivity of the substrate determine the success of the EPD deposition [29]. Lower surface charged particles tend to attract each other and the deposited coating was found to be porous, and particles with a high surface charge produce a strong electrostatic repulsion force at the time of deposition, thereby producing a dense coating. Hence, a uniform particle suspension with a proper conductivity and medium dielectric constant results in better deposition.

6. Coating materials

6.1. Ceramics

The inherent properties of ceramics, including their high compressive strength, compared to metallic materials due to the formation of atomic bonding at elevated atmospheres, and their combination of ionic and covalent bonds, make them suitable for replacing various parts of the body, particularly bone and dental crowns in dentistry [30]. These implantable ceramic materials, termed bio-ceramics are used for the repair and reconstruction of diseased and damaged body parts. They are categorized as bio-inert, bio-reactive and bio-resorbable in reference to their interaction with the biological environment.

Bio-ceramics are generally free from debris and can be designed with properties close to those of bone natural materials. Bio-ceramics of these types are used to produce femoral head components of the ball and socket, an acetabular component of the hip implant. Materials such as silicates, metallic oxides, carbides, and selenides are used in enhanced applications due to their improved physio-chemical properties. Bio-inert ceramic materials have been found to have more mechanical properties than other ceramics. Some ceramics such as glass and calcium phosphates are classified as bioactive ceramics depending on their formation of bonds in physiological solutions. These bioactive ceramics are used mainly as coating materials in orthopedic and dental implants due to their characteristic ability to form bond between the bone and surrounding tissues. Bio-ceramics with low tensile strength and low fracture toughness are limited to use in heavy load applications. These drawbacks can be overcome by using them as coatings on metallic material and for such heavy load applications as joint replacements [31].

6.1.1. Hydroxyapatite (HAP)

Hydroxyapatite [Ca_{10} $(PO_4)_6$ $(OH)_2$] is an important calcium phosphate-based material that has been used in biomedical applications due to their better biocompatibility with the physiological system stemming from its negligible toxicity and inflammation causation. Its poor mechanical properties limit its use as a bone substitute, however, to replace damaged or diseased bone in various applications [32,33]. Hence, it can be used as a coating material for improving and giving an edge to the mechanical properties of stainless steel or titanium alloys to promote bone ingrowth as well as a filling material for correcting amputated bone. Upon implantation, this bioactive material easily achieves an apparent ability to attach to the implant-tissue interface with good osteoconductive behavior by the formation of an apatite layer. According to the need, HAP has been modified to form dense-compact HAP and porous HAP for various biomedical applications. Augmenting HAP with a polymer matrix tends to improve its mechanical strength and bone-bonding ability [32,34] HAP can also be prepared from different waste materials such as egg and snail shells, and the products have been found to exhibit excellent biocompatibility with various osteoblast and fibroblast cell lines [35].

6.1.2. Zirconium dioxide (ZrO_2)

Zirconia is an oxide of zirconium (Zr^{4+}) with a polycrystalline biphasic structure. Zirconia exists in three different phases the mono, cubic and tetragonal, based on the temperature and environment. The existence of different phases gives it greater toughness and strength [36]. Its inherent properties of specific hardness, high wear resistance with a low coefficient of friction, and chemical inertness with an enhanced elastic modulus are thought to improve zirconia's mechanical properties making it a candidate for use in orthopedic and dental applications [37–39]. The better mechanical strength with an enhanced esthetic appearance and lower plaque accumulation of zirconia on implants makes them a better alternative than titanium implants [40,41].

6.1.3. Titanium dioxide (TiO_2)

Titanium dioxide combines excellent resistance to corrosion and superior biocompatibility with photocatalytic activity. These properties make TiO_2 an ideal biomaterial with various ubiquitous applications in pharmaceuticals, pigments and cosmetics, and it has attracted particularly wide usage in the biomedical field as an integrating agent for implant-bone tissues. These ideal properties are due to its physio-chemical properties, including inertness, thermal stability, and an ability to assume various polymorphic forms: anatase, rutile, brookite, and oxygen deficient α-Ti_3O_5 [42,43].

6.1.4. Silica (SiO_2, Bioglass)

Silica (SiO_2) is the dioxide form of silicon, which has been used for many applications due to its covalent bonding between atoms with excellent chemical stability. New research findings have led to the sue of silica-based biomaterials in tissue regeneration and drug delivery applications. First and foremost, Hench et al. (1971) found that bioglass formed tight chemical bonds with bony tissue through the formation of an apatite layer between them. Since the introduction of bioglass, various bioactive glasses and glass-ceramics have been developed [44]. These materials include glass-ceramic A-W (where "A" represents apatite and "W" represents wollastonite), P_2O_5-free $CaOSiO_2$ glass, silicate glass, CaO-SiO_2-P_2O_5 glasses, and MgO-containing glasses. The formation of a hydrated silica gel on the surface is believed to play a key role in apatite formation under both in vivo and in vitro conditions due to its capability of releasing various ions, thereby promoting hydroxyapatite nucleation upon interaction with soft tissue and cell membrane proteins. Silica exists as silica spheres, bioglass, bio glass-ceramics, mesoporous silica gel, silica aerogel, and sol-gel coatings on metallic materials. Due to its direct bone-bonding ability, it has been used to reconstruct bones affected by various bone diseases. Vasconcelos et al. (2000), with sol-gel coatings on silica and Galliano et al., (1998), Vallet-Regi et al. (2001), with SiO_2, SiO_2-CaO, SiO_2-CaO-P_2O_5, studied the effect of coatings on implants to prove their improved adherence and better corrosion-resistance properties in simulated body fluid [45–47].

6.1.5. Zinc oxide (ZnO)

Zinc oxide is a safer highly efficient antimicrobial agent that has found use in food and agricultural systems [48]. In addition to its antibacterial activity, low thermal expansion coefficient, and better lubricity properties, ZnO has been utilized as an additive material to improve coating characteristics with less bacterial contamination on implantable materials such as screw and plate. Its antibacterial properties with their deodorizing ability make them applicable for various products as cotton fabrics, diaper rash preventing agents, antiseptic ointments, and anti-dandruff shampoos [49].

6.2. Composite

A composite is a combination of two or more material with distinct constituents that offers synergistically improved applications with different physical and mechanical properties. Composites, properties such as particle size, surface area, and mechanical properties differ from those of their original constituent materials in ways that make them suitable candidates for various biomedical applications. The mechanical properties of the natural hard tissue are comparatively higher than those of individual ceramic biomaterials. Their mechanical properties are generally weaker, which limits their property limits their usage in high load-bearing applications. Development of various composite coatings such as ceramic-ceramic or polymer-ceramic coatings for metallic implants is producing better mechanical properties with improved biomedical applications.

6.2.1. Ceramic-ceramic composites

Composites consisting of HAP with a bioactive glass coating exhibit superior mechanical strength with greater adhesion than HAP without disturbing its bioactive properties. Various researchers have studied the composites consisting of bioglass-apatite coatings on Ti-6Al-4V [50,51]. Composite made of HAP+ZrO_2 +Y_2O_3 on Ti-6Al-4V in particular revealed improved mechanical properties with greater bioactivity [52]. Composites free from bioceramics (porcelain wollastonite) have also been studied and found to exhibit improved mechanical properties [53]. Furthermore, an in-vivo animal study of HAP and bio-inert alumina composites has been reported to produce excellent osteointegration with bone.

6.2.2. Polymer-ceramic composites

The development of polymer (organic)-inorganic composites produces novel high-performance materials, and their applicability when combined with various inorganic materials such as metal oxides (ZnO, Al_2O_3, TiO_2) and SiO_2 has been studied [54]. A polyetheretherketone (PEEK)/ bioactive glass composite coating on NiTi with uniform deposition for improved adhesion and microstructural homogeneity was developed by Boccaccini et al. in 2006. They found that the presence of the polymeric material PEEK produced excellent tribological and chemical resistance with high strength [55].

7. Conclusion

Conventional surface modification techniques, even recent ones fail to achieve a biocompatible surface covering for metal implants. Corrosion also plays a pivotal role in implant failure that cannot be ignored as it may generate toxicity and produce adverse effects or even damage tissues. Although ceramic-coated metal composites have a great future in biomedical applications, they do come with certain limitations, such as coating thickness, corrosion, degradation, and debris releases. Research efforts should be directed toward further improving and controlling their physiochemical properties for long term, sustainable coatings. Even better, composite coatings on implants can be tuned according to the needs of the host as they provide the opportunity for workability in their composition and properties. The choice of coatings and applicable processes should be made solely based on target tissues and the factors governing the respective tissue regeneration processes.

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