

Advanced Alloys and Coatings for Bioimplants

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Implant materials have significant requirements in medical industries due to orthopedic ailments of elders, fractures caused by accidents, sports injuries, bone replacements, revision in surgeries, change in lifestyle, etc. Contamination of bone and its deterioration is a common problem in patients because of inflammation, improper integration, infections and mechanical instability. Therefore, demand of high efficiency implant is increasing day by day. It is important to design and develop suitable implants with improved properties of mechanical strength, antibacterial, corrosion resistance, hemocompatibility and biocompatible to address those challenges. Implant materials should have proper surface chemistry for long life duration. Metals, ceramics and polymers are promising materials which are extensively used as implant materials. Metallic implants are superior in its mechanical properties, biocompatibility and corrosion resistance, but they are bioinert materials, and this is unable to match with osseointegration properties [1]. It is important to make a note that corrosion of metals are difficult to detect in the form of pitting, cracking, fatigue, fretting, crevices, galvanic etc. which are the major problems inside the liquid medium of body. Titanium (Ti), Ti alloys, stainless steel (SS), magnesium (Mg) alloy, cobalt (Co)-chromium (Cr) alloy, zinc (Zn) alloy, gold, iron (Fe), alloy tantalum, etc., are used as metallic implants. Ceramic materials are specifically used for dental implants such as hydroxyapatite, zirconium oxide, aluminum oxide, tricalcium phosphate, silicates, etc. Surface tailoring on the implant surface plays an important role, mainly to improve the performance and durability.

Temporary implants mainly fabricated by titanium and its alloys are used as pins, plates and screws, and give sufficient support to the damaged bone site for effective bone healing. The temporary implant will be removed after 3–6 months of implantation as it is not necessary to remain inside the body for a prolonged duration. However, it possesses severe challenges while revision surgery takes place. Due to the superior biocompatibility nature of Ti implants, new bone formation will be occurred onto temporary implant surface (pins, plates and screws) by fibroblast and osteoblast cell overgrowth. Still, minor cracks or fracture in the bone site causes severe health issue for the patient, while removing the implants. To overcome this issue, bioinert/hydrophobic coatings play a vital role to prevent cellular interaction and prevent bone overgrowth.

Polymeric implants are defined for cosmetic and artificial meniscus replacement in the form of polyethylene and poly (vinyl alcohol) (PVA) hydrogel, respectively. Hydrated forms of polymers combined with CaPO₄ are used to develop scaffolds. USD 100,000 million has been the reported cost of implant market value, which will increase by 2023 [2]. To achieve all properties in bulk implants is a challenging task since biological activities of body fluid and tissue are not compatible with implants. Better implant surface and its favorable biological response are based on the selection of materials and its pattern of deposition. Osseointegration is a key factor where the implant should have direct contact with the bone [3]. However, this is possible only by implant modifications either through surface treatments [4] or surface coatings [5].



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The prime benefits of the surface treatment of implants are the change in topography of implant materials to obtain better osseointegration. Surface treatments of the implants are prepared by etching process, grit blasting, machined, electropolishing, laser peening, etc. [6], and this is required to improve the bone–implant interface [7]. Acid etching is carried out to enhance osseointegration and stimulate biological properties on implant surfaces [8]. Grit blasting surface treatment is required prior to the plasma spray method to obtain superior adhesion among both the substrate and the powder [9]. The machined process will provide polished or milled implants. Electropolishing onto implants increases the corrosion resistance. However, magneto-electropolishing has more remarkable features such as increased surface hardness and biocompatibility [10]. Laser peening is a grooves-type architecture which is created on implant surface to improve the mechanical and biological reactions with the neighboring biomaterials [11].

Surface coatings or surface modifications are the key success to enhance the osseointegration rate of implant materials to avoid complications raised due to infection inside the body. Hydroxyapatite (HA) coatings enhance the osseointegration properties of implants [12], magnesium coating is significant in developing bone density [13], the addition of zirconium improves the mechanical properties of coated film [14], chitosan has antibacterial and antifungal properties [15], the collagen coating aids in bone regeneration [16], the silver coating will have bacterial colonization control [17] and the antibiotic-loaded hydrogel coating avoids bacterial infections [18]. To achieve the mechanical, durability, corrosion resistance and biocompatibility properties on implant materials, surface modifications by physical vapor deposition (PVD), chemical vapor deposition (CVD), plasma spray, sol–gel and electrodeposition are the most suitable methods. In PVD techniques, atoms, ions and molecules of target materials are deposited onto the implant surface under vacuum conditions and controlled environments to form a protective layer. Evaporation and sputtering are types of PVD which are differentiated based on the selection of materials, atmospheric conditions and ionized gas to achieve the desired composition.

Modified implant surfaces by PVD techniques have excellent strong bonding, uniform dense film layer, corrosion resistance, improved surface hardness and superior biocompatibility fit for the human body [19]. Surface coating was studied by depositing Ag-integrated TiO₂ coatings by thermal evaporation along with micro-arc oxidation to improve the corrosion resistance and bioactivity on the titanium implants [20]. The sputtering process tuned the implants' surface with high mechanical, chemical, thermal properties and osseointegration, mostly with the ceramic materials [21]. The PVD technique is a promising approach for fabricating surface-modified material for wear resistance and scratch resistance coatings, especially for load bearing applications including total knee and hip replacement prostheses. Different coatings materials such as TiN, TaN, TiZrN, WN, WMoN, TiC and ZrC have been used for load-bearing applications.

CVD techniques are a promising method for bio-ceramic coatings with bulk, amorphous, film, single/poly-crystalline and powder materials to achieve controlled crystal phase and microstructure and to improve biocompatibility [22]. Hydroxyapatite powder coating was applied to the metal implants through plasma spray to support bonding between the living bone and the metal implant [23].

Sol–gel coating is performed at low temperature with complex geometries, low-cost method, but it is not much suitable for implant coatings due to low wear resistance and high permeability [24]. Electrodeposition coating is used by the implant industries since fast deposition, uniform coating thickness and morphology can be controlled onto implant materials [25]. Ion implantation process is performed for metal implants at low temperature with direct addition of ions of elements in controlled environment to attain the desired properties. Ceramic coatings are mostly employed for dental implants which include both bioactive (HA and Ca₃(PO₄)₂) and inert ceramics (Al₂O₃ and ZrO₂) [26]. These materials improve both biological as well as mechanical properties of implants. Alteration of polymer coatings on the implant surface is easy and categorized into natural (chitosan, collagen, gelatin, alginate, cellulose) and synthetic polymers such as poly (lactic acid), poly (lacto-co-

glycolic acid), polydopamine, etc. [27]. Polymer coatings on implants are mostly performed by sol–gel, dip coatings, spin coating, electrospinning, etc. These polymers are mostly used for organ regeneration onto implants, but there is a possibility of in vivo inflammation at some point of degradation [28].

Many implant materials are susceptible to bacterial adhesion where Cu, Ag, Zn nanoparticles and other antibiotic materials which have biocidal properties are incorporated in surface-modified film. Hybrid implant coatings are prevalent as two dissimilar materials have different function, chemistry and biocompatibility which serve as protective layers with smart multifunctional properties. Nanocomposite coatings of hydroxyapatite along with carbon nanotube, zirconia, bioactive glass, chitosan, TiO₂, collagen, etc., is investigated to avoid the problems related to HAP. Nanocomposite of alumina, graphene and hydroxyapatite coatings were carried out on Ti–6Al–4V alloy of bone implant to increase tribo-mechanical and antibacterial properties [29]. There are many other complications of surface-modified implants which have been noticed because of poor integration of implants, mechanical instability and infections.

Additive manufacture (AM) is used to print the fabricated materials based on the size of implants. Three-dimensional printing technology of bioprinting is booming, and it has great potential in implant industries. Bioinert metallic materials are widely used by the medical industries in 3D printing technology, but the usage of cellular components is still in its infancy stage. This technology customized the implant manufacture based on the patient's requirements with enhanced properties. Three-dimensional materials should be biocompatible, less toxic, and the materials should not leach to the body; moreover, its requirements should match based on the implant location in the body. Techniques implemented to manufacture 3D implants are based on selected materials. Fused deposition modeling (FDM) and Direct-Ink-Writing (DIW) methods are used to manufacture polymers and ceramic implants. Stereolithography (SLA) techniques are applied on liquid resin to harden it by laser light. The use of high-power lasers involved in melting the metallic powders and binding them to make an implant model is known as selective laser melting (SLM). By employing high-energy beams of electrons under vacuum conditions, melting of metallic powder is another way of molding implants and it is determined as the Electron Beam Melting (EBM) method. However, each method has its own limitations in modifying bioimplants.

It is important to manufacture customized implants subject to individual requirements. For an instance, patients with poorly controlled diabetic mellitus and osteoporosis patients who undergo orthopedic implant fixations are likely to have complications with implant-associated infections, reduced level of bone–implant contact and diminish response to healing which severely affects successful rate of implants (successful rate is 64%), particularly, beyond 50 years of age group. To address the present challenge, surface tailoring on orthopedic implant is an effective way to improve the successful rate of implants as well as giving better solution to implant surgery patients who has diabetes mellitus and osteoporosis diseases. A bioactive glass coating on the implant surface is a crucial approach, mainly to accelerate osteogenesis, forming new blood vessels in its surrounding tissues and wound healing ability in orthopedic applications.

Furthermore, the intensive investigations are being carried out through more advanced techniques to address future requirements of patients and its particular applications.

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