*Safa Jabbar[1], Shaymaa Abbas Abdulsada[1]**

[1]Department of Materials Engineering, Faculty of Engineering, University of Kufa, Iraq

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Investigating the effect of biomaterial coating deposited electrophoretically on titanium and its alloys substrates: a review

ABSTRACT

The current study discusses the value of improved biomaterials, particularly coatings for titanium and its alloys employed in surgicalsettings. Demonstrates how coating processes like electrophoretic (EPD) can be used to enhance mechanical and biological qualities of these materials. Because titanium is lightweight and resistant to corrosion, it is a preferred material for medical implants used in tissue repair and fracture treatment. The study also analyzes the use of ceramic coatings like hydroxyapatite and TiO_2 in promoting bone regeneration, as well as issues with biocompatibility and tissue adhesion that arise in metallic implants. Positive outcomes indicate that advancements in biomaterials can enhance treatment results and augment the efficacy of medical implants, hence augmenting patients' quality of life.

Keywords:*Bio-coating, Titanium, Anti-corrosion alloys,Electrophoretic deposition.*

1. INTRODUCTION

The use of bio-active metallic materials in medical treatments can be traced back to nearly twenty years ago.About 70 to 80% of the devices used in the medical field are made from bio-compatible materials. Metallic bio-materials are of great importance in fracture fixation, bone repair, and the treatment of damaged tissues, especially hard tissues, which contributes to improving the quality of life for patients. This is due to its great strength, durability, and toughness. The need for bio metallic materials with superior mechanical properties is significantly increasing due to the growing number of elderly people worldwide, as older adults face a higher risk of hard tissue failure [1].

In the early stages of developing metal implants, there were challenges related to corrosion and reduced strength. The choice of the type of metal used in biomedical applications depends on the specific uses of these implants. Table 1 provides a summary of the different types of metals commonly used in various classifications of implants [2].

*Corresponding author: Shaymaa Abbas Abdulsada
E-mail: shaymaa.radhi@uokufa.edu.iq

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Due to their high strength, durability, and low wear rate within the body, implant materials such as titanium, stainless steel, cobalt, and their alloys are frequently used in orthopedic and dental applications [3]. Figure 1 shows many typical applications for metal implants [4].

Titanium alloys are widely used in dental implants and bone grafting, as well as in other devices such as plates and screws, thanks to a range of distinctive properties, including good bio-compatibility, resistance to corrosion and wear, excellent mechanical properties, and effective osseointegration. Porous titanium alloys have been developed as an alternative to orthopaedics materials, providing good biological fixation through the growth of bone tissue within the porous network [5].

Despite the numerous benefits that titanium materials offer, there are concerns regarding their adequate stability and ability to resist corrosion in the body's fluid environment, especially in the long term. The release of corrosion products can lead to metallosis, which in turn may cause loosening of the implant or deterioration of its properties [6]. Furthermore, rejection of some internal prosthetics by the recipient may occur shortly after surgery due to an allergic reaction [7].

In addition, the implant should have a suitable micro-structure that enhances the formation of a permanent bond between the tissue interface and the implant [8].

Table 1. Classification of implants and types of metals used [2]

Division	Example of implants	Type of metal
Cardiovascular	Stent Artificial valve	316L SS; CoCrMo; Ti Ti6Al4V
Orthopaedics	Bone fixation (plate, screw, pin) Artificial joint	316L SS; Ti; Ti6Al4V CoCrMo; Ti6Al4V; Ti6Al7Nb
Dentistry	Orthodontic wire Filling	316L SS; CoCrMo; TiNi; TiMo AgSn(Cu) amalgam, Au
Craniofacial	Plate and screw	316L SS; CoCrMo; Ti; Ti6Al4V
Otorhinology	Artificial eardrum	316L SS

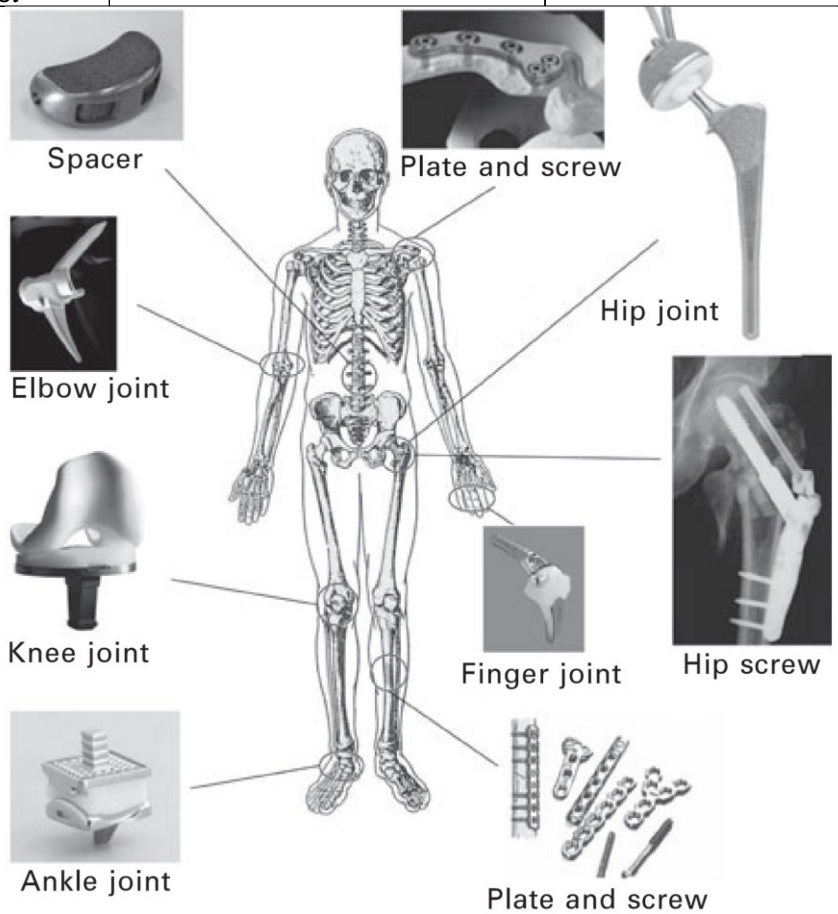


Figure 1. Biomaterials for human application [4]

Based on what has been mentioned earlier, methods are being explored to modify the surface of metal implants in order to meet these requirements, particularly concerning long-term aspects. The following methods that have already been used can be identified: thermal plasma spraying [9], plasma spray [10], physical vapor depo-sition[11], sol–gel [12], ano-dic oxidation (AO) [13], micro-arc oxida-tion (MAO) [14], and electro-phoretic deposition (EPD) [15].

The last three methods mentioned fall under the category of electro chemical methods, which are characterized by their simplicity and relatively low cost compared to the other methods mentioned. Furthermore, this process contributes to facilitating the production of coatings with diverse structures, roughness, crystallization, chemical composition, and wettability, in addition to properties such as corrosion resistance and mechanical characteristics on materials of various shapes. The equipment used in this context is also considered cost-effective [16].

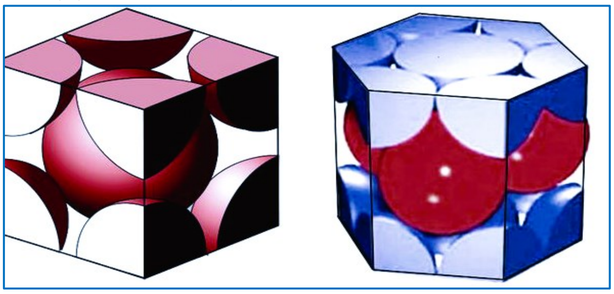
The popularity of electrophoretic deposition (EPD) is increasing as an effective method for processing biomaterials, especially in the field of bio active coatings and nano structures used in medicine[17].HA has been an attractive option for a long time as a partial alternative to bone, due to its similarity to the mineral component of natural bone.The synthetic hydroxyapatite (HA) material has shown excellent biocompatibility in the laboratory with cultured osteoblasts, as well as other cell types, which grow easily on HA compounds or surfaces coated with it. Hydroxyapatite (HA) is considered a bioactive ceramic that promotes bone growth; however, it suffers from relatively weak mechanical properties [18].

To improve the mechanical properties of hydroxyapatite (HAp) and to produce coatings with better bio-activity and enhanced mechanical properties, another type of bio-ceramic material is combined with HAp, such as titanium dioxide (TiO2), which is considered one of the other inactive bioceramics.

Titania is characterized by exceptional corrosion resistance in body fluids, as well as high fracture strength and significant load-bearing capacity, with a sufficient level of wear resistance [19,20]. Also it is a bio compatible material that is compatible with living organisms and is characterized by its biological activity, as it possesses antibacterial activity and effective properties against fungi [21].

2. TITANIUM AND TITANIUM ALLOYS

Titanium (Ti) is a shiny metal with a silver color. It is characterized by a high strength of up to 430 MPa and a low density of 4.5g/cm^3, while iron has a strength of 200 MPa and a density of 7.9 g/cm^3. Therefore, titanium has the highest strength-to-density ratio among all other metals. Furthermore, titanium is characterized by a relatively high melting point exceeding (1650°C or 3000 °F), and it is also a paramagnetic material with relatively low electrical and thermal conductivity. This metal exists in two different crystalline forms known as body-centered cubic (bcc) and hexagonal close-packed (hcp) structures, as shown in Figures 2 (a) and (b), respectively [22].



a) b)

Figure 2. Crystalline state of titanium: (a) bcc, and (b) hcp [22]

At low temperatures, pure titanium is characterized by a close-packed hexagonal structure known as alpha titanium (α titanium).At high temperatures, the stable structure is the body-centered cubic (bcc) structure, known as titanium β [23].

2.1. Effect of alloying elements on titanium properties

In titanium alloys, three types of alloying elements are generally utilized: neutral elements, α -stabilizers, and β-stabilizers. In titanium alloys, elements like N, Al, O, and C are referred to as α-stabilizers because they generate the α phase [24-26].While components that yield the β phase are categorized as β-stabilizers. β-stabilizers can be classified into β-eutectoid and β-isomorphous elements according to the alloying elements that are added to titanium.

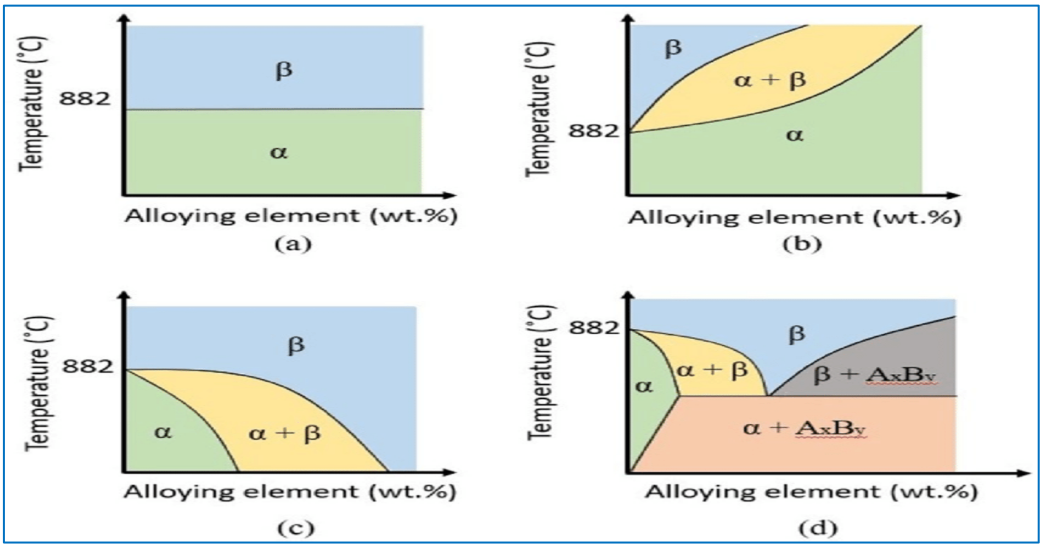


Figure 3. Different titanium alloy stabilizer types (a) neutral, (b) α-stabilizing, (c) β-stabilizing (isomorphous) and (d) β-stabilizing (eutectoid) [27]

As shown in Figure 3 isomorphs elementssuch as tantalum (Ta), molybdenum (Mo), vanadium (V), and niobium (Nb) are highly soluble in titanium. Nevertheless, eutectoid elements—manganese (Mn), chromium (Cr), silicon (Si), iron (Fe), cobalt (Co), nickel (Ni), and copper (Cu)—show extremely little solubility in titanium and are more likely to form intermetallic compounds with other elements. Conversely, elements with almost little influence on the α/β phase border, such as tin (Sn), hafnium (Hf), and zirconium (Zr), are regarded as neutral elements [27-32].

Titanium alloys are predominantly recommended for implant fabrication due to their exceptional corrosion performance. Table 2 shows the different stabilizing elements added to titanium alloy to stabilize particular structure and improve properties of titanium alloys [33-38].

Table 2. Titanium alloy stabilizer with its effects and different properties [38]

Stabilizing elements	Impact on transition temperature	Effects on properties of Ti
α-stabilizer :Fe, Mo, Ni, V, Cr, Nb	Increase	Hardening
β-stabilizers : N, Al, O, C	Decrease	Grain refiners
Neutral elements: Zr and Sn	No noticeable impact	Hardening

3. CORROSION RESISTANCE OF TITANIUM AND TITANIUM ALLOYS

The natural breakdown of metals and alloys brought on by interactions with the environment that are chemical, biological, and electrochemical in nature. Conditions that might cause corrosion include high pressure, heat, humidity, oxygen, inorganic and organic acids, and chlorides [39].

Metals are destroyed by corrosion, which turns them into oxides or other corrosion products. Because corrosion causes parts or buildings to become unusable, it reduces the amount of earth's material resources that can be used to replace them, which has an impact on the world's metal supply [40]. The high corrosion resistance of titanium alloys is due to the presence of a thin oxide layer that adheres to their metallic surface. This film naturally forms when titanium alloy is exposed to air or oxygen-rich environments, due to the close relationship between titanium and oxygen. Due to this fact, the oxide film can be easily repaired even in the presence of oxygen at low partial pressures (ppm) when it is subjected to damage. Although the oxide layer that covers titanium and its alloys has a high level of stability, when these materials are used in agriculture, electrochemical reactions may occur with physiological fluids. These reactions are exacerbated by the interplay between corrosion and mechanical stresses and/or wear [41].

4. SURFACE MODIFICATION TECHNIQUES

It has become extremely necessary to prevent the corrosion of biomaterials, especially to address the infections and allergic reactions that may arise from the implantation of these materials in the human body.Due to the issue of corrosion, a set of techniques has been adopted to modify the surface with the aim of improving corrosion behavior. The introduction of surface modifications on biocompatible metals is considered the "optimal solution" so far to enhance corrosion resistance performance, as well as to achieve superior biocompatibility and promote bone integration of biocompatible metals and alloys. Biocompatible metals include processes such as coating deposition, the development of a passivation oxide layer, and ion beam surface modification [42].

The acceptance of the biomaterial by the human body is the primary criterion for selection. When the material is implanted, it shouldn't have any negative side effects—such as allergies, inflammation, or toxicity—either right away during surgery or in the following[43]. Biomaterials can be modified via a variety of commonly employed surface modification techniques, including covalent grafting, surface coatings and synthetic films, plasma treatment, and self-assembled monolayers (SAMs) [44].

4.1. Coatings for titanium and its alloys in biomedical applications

Metal implants may sometimes fail in surgical procedures due to several factors, including insufficient biocompatibility, high degradation rates (as seen with magnesium alloys), inflammatory response, infection, inertness (such as with stainless steel, titanium, and cobalt-chromium alloys), as well as low wear resistance, mismatch in elastic modulus, excessive wear, and the presence of hidden stress. Therefore, it is important to address this issue by developing a method that contributes to improving the vital functions of metallic implant surfaces, by modifying the surface and shape of the materials without affecting the mechanical properties of the metallic implants as shown in Figure 4.

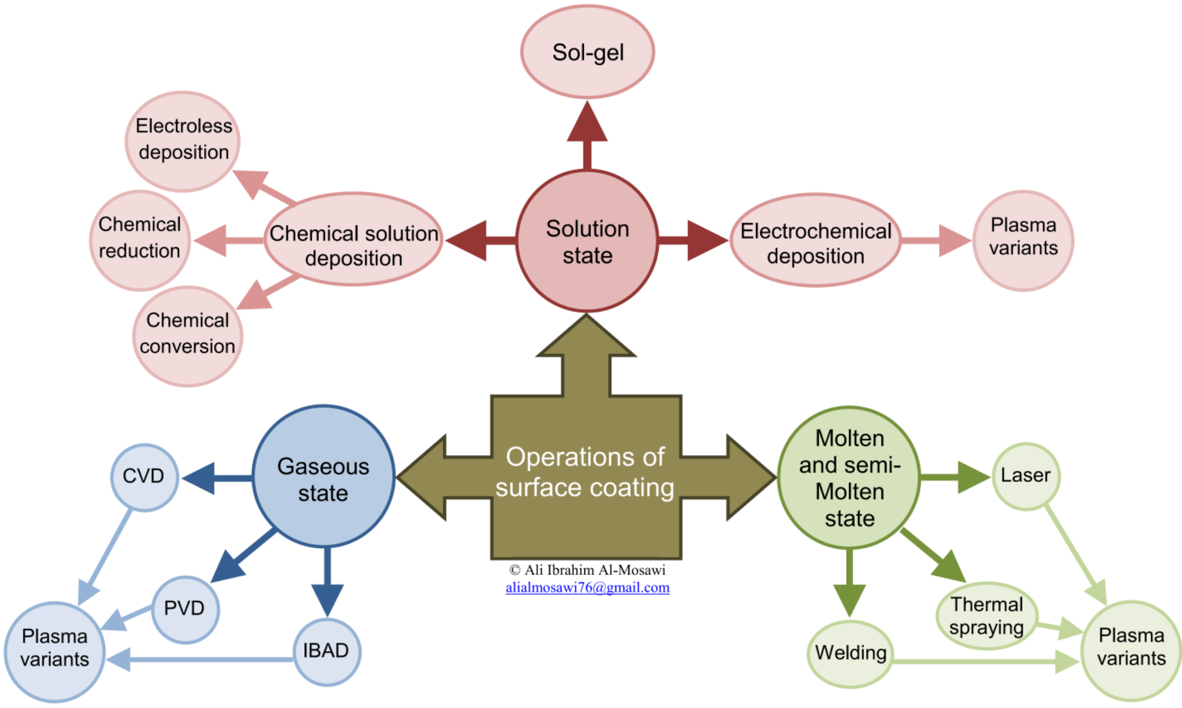


Figure 4. A broad division of surface engineering methods

The process of surface modification of metals through the use of coatings is considered one of the effective methods for enhancing the performance of implant materials, among the many available techniques [45]. By virtue of their reliability and efficiency, ceramic coatings are considered the optimal choice for activating implants that come into direct contact with bones and tissues. This is due to their unique properties that enhance bone compatibility and provide high stability [46,47]. The surface modification process using coatings can enhance the antibacterial activity of biomaterials. Coated surfaces contribute to improving the attachment of peptides to cells, directing changes in host cells, as well as extracellular matrix (ECM) proteins and tissue growth, leading to further improved acceptance of biomaterials. Coating of Ceramics on biomaterials show promising results in the field of orthopedic surgery, as they play an important role in enhancing bone regeneration and repair [48].

4.1.1. Hydroxyapatite Coating

Hydroxyapatite (HAp) is a natural mineral form of calcium apatite, characterized by the chemical formula Ca5(PO4)3(OH). It is often expressed in the formula Ca10(PO4)6(OH)2 to indicate that the crystal unit cell consists of two molecules. The HAp crystal structure unit cell, which is made up of Ca, PO4, and OH groups densely packed together, is depicted in Figure 5 [49].

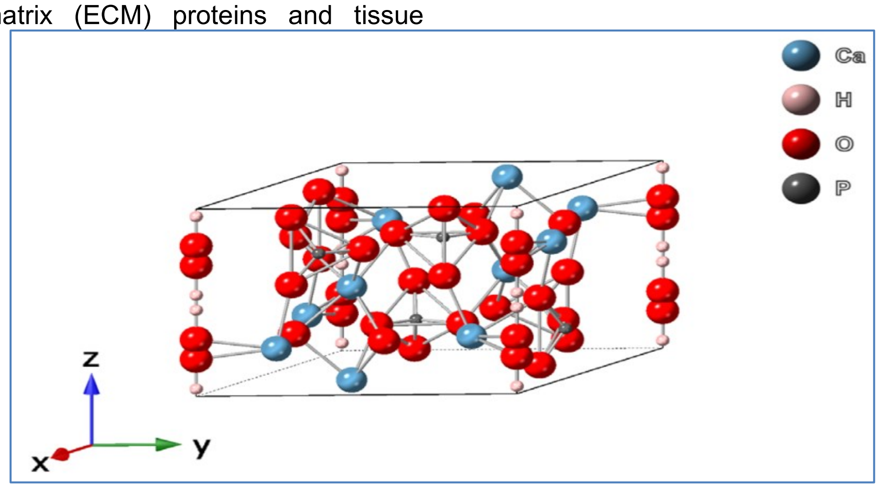


Figure 5. The hydroxyapatite molecular structure: a unit cell perspective on the hexagonal crystal structure [49]

Hydroxyapatite is the main component in the structure of tooth enamel and bone minerals, contributing to their hardness. Hydroxyapatite is used in many fields due to its excellent biocompatibility and active properties. In the field of medicine, it is used in orthopedics and dental implants due to its structural similarity to the minerals found in bones [50].

4.1.2. Titanium Oxide Coating

The oxide of titanium that occurs naturally is called titanium dioxide (TiO_2). It is sometimes referred to as titania. One of the most widely used ceramic materials in applications including sensors, photovoltaics, self-cleaning glass, water purification, photo-catalyst, and corrosion protection coatings is titania in its several crystalline forms. Titania is utilized so effectively in all these industries as a thin or thick coating film primarily due to its high chemical durability and thermal stability [51].

Titania exists in three primary crystalline phases: rutile, anatase, and brookite. These phases can exist as nanomaterials, and the grain size affects how stable they are. Whereas anatase titania is commonly utilized as spherical particles with a diameter of about 20 nm, rutile is regularly employed as a white pigment in polymers with particles size ranging from 200 to 300 nm [52].

All polymorphs, as illustrated in Figure 6 feature distorted TiO_6 octahedral formed by titanium cations six-fold coordinated to oxygen anions. These structures are connected by sharing the octahedral edges (some also have corner sharing). TiO_6 octahedral building block arrangement reveals the crystal formations of titania [53].

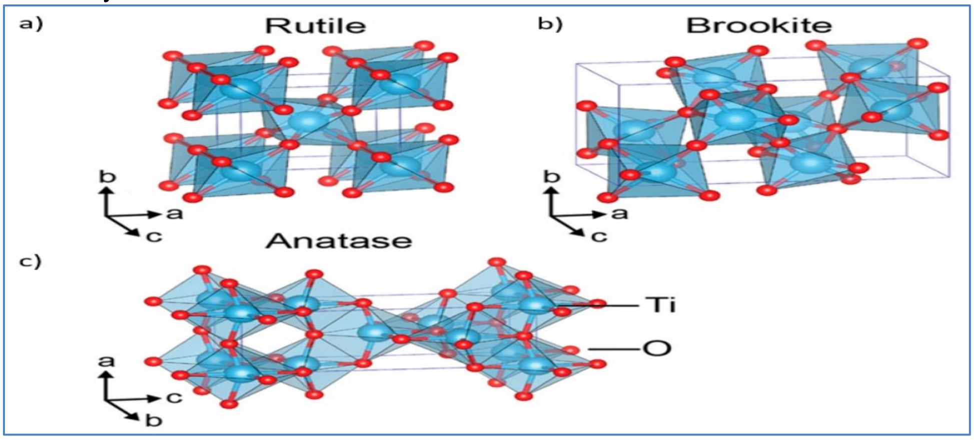


Figure 6. Polymorphs of TiO_2 crystal structures:(a) Rutile, (b) Brookite and (c) Anatase [53]

5. ELECTROPHORETIC DEPOSITION METHOD

EPD is a bridge that connects two processes: deposition and electricity [53].The EPD method is a versatile approach that may be used to deposit a wide range of materials, including composites, metals, ceramics, glasses, and polymers. This is an economical solution that doesn't require expensive equipment. The EPD's widespread use can be attributed to its simplicity in regulating the morphology and thickness of the coatings it forms by accurately adjusting process parameters [55, 56].

The EPD process includes fundamentally three steps [57]:

Creating a steady particles suspension.

- The particles move towards the deposited pole by the effect of the electric field.
- The deposition of particles on the surface of the electrode.

Figure 7 illustrates a graph that shows these steps in the EPD process.

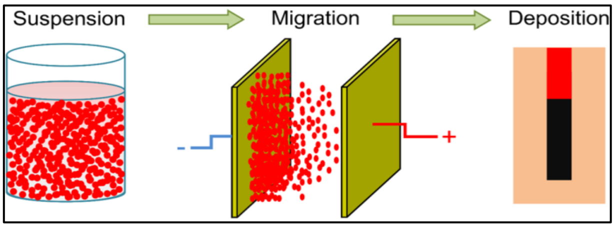


Figure 7. The EPD steps are depicted schematically [57]

The main difference between the electrophoretic deposition (EPD) process and the electrochemical deposition (ELD) process is that the former relies on the presence of suspended particles in a solvent, while the latter depends on the use of a solution containing salts., i.e. The positive and negative ions [58]. There are two basic types of EPD processes: cathodicEPD and anodic EPD. CathodicEPD is the process by which positive charges are deposited on the cathode (negative electrode).and anodic EPDis the accumulation of negative charges on the anode, or positive electrode. As depicted in Figure 8 [59].

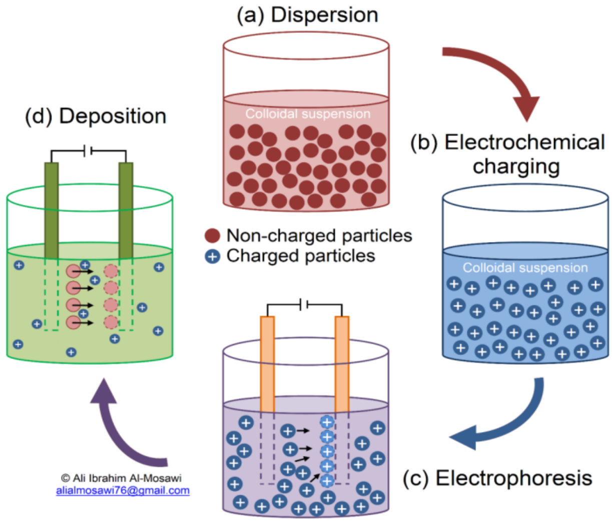


Figure 8. Schematic of the procedure for electrophoretic deposition [59]

6. BIOCOATINGSEFFECTS ON BONE REGENERATION, TISSUE ADHESION AND BIOCOMPATIBILITY OF TITANIUM ALLOYS IMPLANTS

The primary criteria for choosing a coating material are (a) sufficient mechanical dependability, adhesion strength, and fracture toughness to endure the applied forces; (b) resistance to corrosion in bodily fluid environments; and (c) biocompatibility and absence of inflammation, toxicity, or other undesirable effects. Biomedical coatings can be categorised into three primary classes based on how well they function in the organism: bioinert, bioactive, and bioresorbable. Bioactive coatings, as opposed to bioinert, are biomaterials that have the ability to promote the regeneration of surrounding tissue and cells around the foreign graft and the release of bioactive chemicals to eliminate post-operative problems. Absorbable (bioresorbable) coatings are made to dissolve electrochemically in the human body and then be metabolised by tissue and cells [60-65].

Improving the metal implant surface's osteo-conductive, osteo-inductive, and osteogenic properties is the primary goal of applying a biocompatible coating. Osteo-inductivity is the ability of the surface to promote the differentiation of precursor (stem) cells into osteoblasts, whereas osteo-conductivity is the coating's capacity to serve as a scaffold for the production of extracellular bone matrix where osteoblasts can adhere and multiply. In order to calcify the collagen matrix of the freshly produced bone structure, osteoblasts are alloyed to produce calcium nodules [66-70].

Because of its strong mechanical qualities, antibacterial and catalytic activity, and long-term durability against chemical and photocorrosion, TiO_2 is a valuable material for biomedical applications. When immersed in SBF solution, TiO_2 can encourage the surface to develop calcium phosphate or bone-like apatite, making it appropriate for bone replacement and reconstruction. Furthermore, it was discovered that the anodisation of TiO_2 coating on the surface of Ti substrates was a successful technique for lowering the implant's temperature rise during microwave diathermy treatment, which could offer a potential rehabilitation option for internal bone fracture fixation. Like TiO_2, tantalum oxide (Ta_2O_5) may promote the quick attachment of soft tissue and bone and aid in the creation of bone-like apatite. The magnesium alloy's in vitro biocompatibility and early-stage corrosion resistance were both improved by tantalum oxide made by reactive magnetron sputtering. When coated using a twin-gun magnetron sputtering method, a Ta_2O_5 coating containing 12.5%Ag demonstrated both good cellular biocompatibility with skin fibroblast cells and enhanced antibacterial activity against S. aureus [71-73].

Since different metal ions (Ca^{2+}, Sr^{2+}, Mg^{2+}, etc.) have been shown to have the ability to enhance osseointegration, grafting metal ions and compounds is another popular technique to increase the osteogenic ability of oxide coatings. Figure 9 provides an example of how different metallic ions affect the numerous processes involved in bone repair [74].

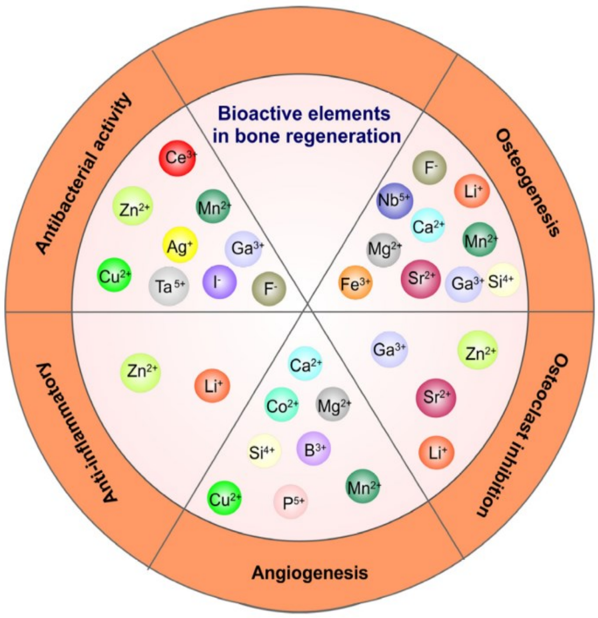


Figure 9. Some ions' therapeutic effects include angiogenic, osteogenic, anti-inflammatory, and antibacterial action [60]

Various photosensitisers can be used to alter the surface of TiO_2 in order to produce reactive oxygen species (ROS) that will kill bacteria when exposed to near-infrared (NIR) light. To increase biocompatibility, hydrothermally generated MoSe2 nanosheets were placed on the surface of porous micro-arc oxidation (MAO) -prepared TiO_2 coatings, and chitosan was applied by electrostatic bonding. Chitosan enhanced the hybrid coating's hydrophilicity and biocompatibility, promoting osseointegration even in the presence of infection under NIR light. Under NIR irradiation, the coatings showed excellent in vivo and in vitro antibacterial properties against S. mutans due to the synergistic effect of hyperthermia and ROS generation. To alter the surface of composite collagen/polydopamine/TiO_2 coatings on Ti implants made by MAO and hydrothermal treatment, Han and co-authors choose MoS_2 because of its broad spectrum response [75-80].

7 .CONCLUSIONS

This review provides a complete analysis to the properties of titanium and its alloys, as well as the impact of surface modification on medical implants used in orthopedic and dental implants and other applications. The analysis focuses on how these modifications extend the life of the implant in the body, achieve biocompatibility, and enhance osseointegration. This is done by coating these alloys with hydroxyapatite and titanium dioxide, as these coatings are characterized by their high corrosion resistance and excellent biocompatibility.

Electrophoretically deposition is one of the most popular methods due to its versatility, simplicity and low cost. The electrophoretic process is affected by a number of factors, including the deposition time, the type of solution, and the voltage used in the deposition process. Biomaterials have several difficulties, such as biocompatibility, durability, and corrosion. Comprehending the ways in which these variables impact the overall functionality of implants might facilitate the creation of novel materials that satisfy the requirements of patients. Biomaterials have several difficulties, such as biocompatibility, durability, and corrosion. Comprehending the ways in which these variables impact the overall functionality of implants might facilitate the creation of novel materials that satisfy the requirements of patients. This research is very important for the future since collaboration between scientists and engineers in this field can lead to tremendous progress in enhancing the quality of life for patients. In summary, the findings show that in order to satisfy the increasing demand, further research in the area of biomaterials is required, with an emphasis on developing coating and surface modification methods.

Data Availability Statement

Statement for Data available on request from the authors: The data that support the findings of this study are available from the corresponding author upon reasonable request.

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IZVOD

ISTRAŽIVANJE UTICAJA PREMAZA BIOMATERIJALA NANEŠENOG ELEKTROFORETSKI NA PODLOGE TITANIJUMA I NJEGOVIH LEGURA: PREGLED

Sadašnja studija govori o vrednosti poboljšanih biomaterijala, posebno premaza za titanijum i njegove legure koji se koriste u hirurškim postavkama. Demonstrira kako se procesi oblaganja kao što je elektroforetski (EPD) mogu koristiti za poboljšanje mehaničkih i bioloških kvaliteta ovih materijala. Pošto je titanijum lagan i otporan na koroziju, on je poželjan materijal za medicinske implantate koji se koriste u popravci tkiva i lečenju preloma. Studija takođe analizira upotrebu keramičkih premaza poput hidroksiapatita i TiO2 u promovisanju regeneracije kostiju, kao i probleme sa biokompatibilnošću i adhezijom tkiva koji se javljaju kod metalnih implantata. Pozitivni rezultati ukazuju na to da napredak u biomaterijalima može poboljšati rezultate lečenja i povećati efikasnost medicinskih implantata, čime se povećava kvalitet života pacijenata.

Ključne reči: *biopremaz, titanijum, antikorozivne legure, elektroforetsko taloženje*

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Shaymaa Abbas Abdulsada: ***https://orcid.org****/0000-0001-7006-2950*
Safa Jabbar: ***https://orcid.org****/0009-0004-4836-7925*