Materials Today: Proceedings xxx (xxxx) xxx

Contents lists available at ScienceDirect

Materials Today: Proceedings

journal homepage: www.elsevier.com/locate/matpr

Surface modification techniques of titanium and titanium alloys for biomedical dental applications: A review

Alekh Kurup [a,*], Pankaj Dhatrak [b], Neha Khasnis [a]

[a] Department of Mechanical Engineering, MAEER'S MIT, Pune 38, India
[b] School of Mechanical Engineering, Dr. Vishwanath Karad, MIT-WPU (Formerly MAEER'S MIT), Pune 38, India

ARTICLE INFO

Article history:
Received 4 May 2020
Received in revised form 7 June 2020
Accepted 11 June 2020
Available online xxxx

Keywords:
Coatings
Implant
Osseointegration
Surface modification
Titanium

ABSTRACT

The materials used for biomedical applications include metal and their alloys, polymers, and ceramics. Of these, titanium (Ti) and titanium alloys are widely used as implant materials owing to its superior corrosion resistance and high mechanical strength. Although titanium has several advantages, being biologically inert, it cannot osseointegrate with the human cells. Thus, the surface of the titanium implant has a very important role, as it determines the rate of osseointegration and the success of the implant. The main objective of this review is to offer a thorough and detailed description of the most promising techniques used for the surface modification of titanium dental implants. A systematic classification of these methods is provided, followed by their advantages. Mechanical methods like acid etching and grit blasting, hydrogen peroxide treatment, acidic treatment, nitride coatings, hydroxyapatite coatings, metal oxide coatings and silver coatings have been analyzed and selected for this review. These methods have been experimentally proven to enhance the osseointegration rate, improving the biocompatibility and stability as well as the antibacterial properties of the implants. Thus, the surface modification of the titanium implant surface significantly improves the properties of the implant. However, further research is necessary to study the implant surface and the human cell interface in more detail and develop new surface modification techniques to manufacture implants with superior properties.

1. Introduction

In recent times, there has been a substantial increase in the development of numerous biomedical materials for a variety of potential applications. These biomaterials are so called because they possess suitable properties to remain in contact with the human cells for extended periods [1]. Such biomedical materials are developed to be used as dental implants, orthopedic and cardiovascular implants, drug delivery devices and so on [2]. The requirement of such materials is that they should be biocompatible i.e. not produce any harmful effects on the human body. Biomaterials generally consist of metals and their alloys, polymers and ceramics. Metals and their alloys are generally used as biomaterials due to their superior mechanical properties and biocompatibility potential [3–5]. Significant research has been conducted on the development of polymers [6–8] and ceramic materials [9,10] used for biomedical applications.

A dental implant is a surgical component, most commonly a titanium post, which supports and allows mounting replacement teeth. Once the implant is mounted into the jaw, it osseointegrates with the human bone and provides a stable support. Titanium (Ti) is used extensively in the medical field as dental implants. This increased usage can be attributed to the low elastic modulus of Ti along with suitable other mechanical properties like tremendous corrosion resistance. Another advantage of using Ti alloys for medical applications opposed to other metallic alloys like the silver-palladium-gold-copper alloy is the increasing cost of Palladium (Pd) and Gold (Au). A titanium oxide layer is formed on the surface of the implant when it is exposed to air. The excellent properties of the titanium implants depends on the structure and chemical stability of this TiO_2 layer, which has a thickness in the magnitude of a few nanometers. Titanium is also used for applications such as orthopedic implants and cardiovascular implants. Titanium, being

---

* Corresponding author.
E-mail address: alekh.kurup@gmail.com (A. Kurup).

https://doi.org/10.1016/j.matpr.2020.06.163
2214-7853/

Please cite this article as: A. Kurup, P. Dhatrak and N. Khasnis, Surface modification techniques of titanium and titanium alloys for biomedical dental applications: A review, Materials Today: Proceedings, https://doi.org/10.1016/j.matpr.2020.06.163

highly corrosion resistant, stays relatively unchanged when it is inserted into the human body as implants, and this property makes titanium biologically inert. Thus, titanium cannot osseointegrate with the human bone cells. Moreover, titanium also possesses lower wear and resistance to abrasion, as its hardness value is low. Surface modification of the titanium surface is necessary, as these properties cannot be infused into the metal during the manufacturing stage. Thus, surface modification techniques are required so that the bone formation and bonding process on titanium and titanium alloys is accelerated [11].

The Grand View Research assessed and valued the global dental implant market at around USD 4.6 billion in 2019, with an expected growth rate 9.0% CAGR. Increasing popularity of dental implants, prosthetic demands and increasing number of dental injuries are some of the key factors for this estimated growth. Of these dental implants, titanium holds the largest market share due to its several benefits. Therefore, there is a greater need to produce Ti implants that have improved life. The surface modification of the titanium implant plays a vital role in this matter and it has been found to significantly improve the biocompatibility and antibacterial activity of the implant.

This paper is structured to first explain the concept of osseointegration and then discuss about how the implant surface and surface modification techniques help in improving the osseointegration rate. In this review, the focus is mainly on some of the most promising techniques for the surface modification of titanium implants: mechanical methods like acid etching and grinding as well as coatings like hydrogen peroxide treatment using fluoride (F) and chloride (Cl) ions [12], hydroxyapatite [13,14], nitride [15,16], metal oxides [17–19] and silver [20,21]. These methods have been experimentally shown to improve the various properties of the titanium implant, making it more suitable to be inserted into the human jawbone. As the current trend shows a substantial increase in the use of titanium implants, it is becoming increasingly necessary to develop methods that would improve long-term usage of these implants. The properties that have been observed to be the most crucial for the success of the implants are the rate of osseointegration, the roughness of the titanium implant surface and finally the antibacterial property of the implant.

2. Osseointegration and relationship with surface modification

Osseointegration has been defined as the direct connection between the human bone and the implant. This plays a key role in implant stability and ensures the success of the implant [23]. In case of the natural tooth, there are several periodontal ligaments that are present between the root of the tooth and the surrounding bone which support the tooth (Fig. 1(a)). However, in the case of implants, they are in direct contact with the bone, there are no periodontal ligaments (Fig. 1(b)). Once the implant is inserted into the bone, the bone grows around the porous structured implant. Once osseointegrated, the implant becomes as flexible and strong as a natural tooth. However, the process of osseointegration can take a long time, usually ranging from a few weeks to a few months. The entire process of osseointegration can be divided into four phases: Hemostasis, Inflammation, Proliferation and Remodeling [24]. Several studies have been conducted to study the different methods to augment the surface properties of the dental implant, thus enhancing the osseointegration rate. Guglielmotti et al. conducted several experiments to study the factors affecting osseointegration. It was observed that surfaces having higher roughness and waviness, which enhanced osseointegration [25]. When the surface properties of the implant are improved, it helps in improving the bonding between the bone and the implant, improves the corrosion and wear resistance of the implant, and makes the implant more biocompatible [26]. In order to osseointegrate with the human bone, the surface of titanium implant has to be modified. Dental implants with rough surfaces have been experimentally shown to have increased bone fixation and Bone-to-Implant Contact (BIC) percentage than commercially available implants [27].

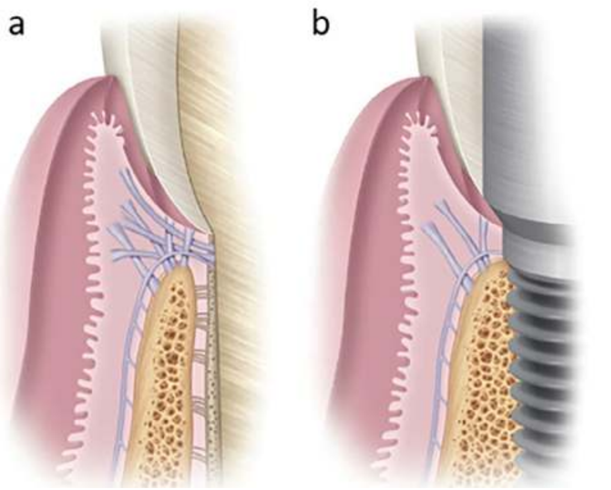

Fig. 1. (a) Tissues surrounding a natural human tooth (b) Osseointegration of implant with the bone [22].

3. Requirements of surface modification techniques

i. Prevent bone formation:

Titanium implants form a layer of calcium phosphate when implanted into the human bone. This improves the hard-tissue compatibility of the implant, but it also leads to increased bone formation. When these alloys are removed from the bone, it leads to re-fracture of the bone. Thus, it is necessary to employ surface modification techniques that do not lead to bone formation [28].

ii. Adhesion to soft tissue:

When the implant does not fully adhere to the soft tissue, it can cause inflectional diseases as well as inflammation, known as “Implantitis”. This can cause failure of the dental implant. Thus, surface modification techniques that help in improving the adhesion of dental implants to the soft tissue are required.

iii. Prevent biofilm formation:

A biofilm is formed when the bacteria invade the implanted site, further leading to the multi-layered formation of bacteria, causing infections like per-implantitis. Thus, it is necessary to inhibit the biofilm formation.

iv. Increase the wear resistance of the implant.

4. Surface modification techniques

4.1. Mechanical methods

The goal of mechanical methods for the surface modification of titanium implants is to alter the surface morphology of the implant, as this will improve the bonding of the implant with the bone. The methods used for this purpose are grinding, machining,

Please cite this article as: A. Kurup, P. Dhatrak and N. Khasnis, Surface modification techniques of titanium and titanium alloys for biomedical dental applications: A review, Materials Today: Proceedings, https://doi.org/10.1016/j.matpr.2020.06.163

blasting and polishing [29]. These methods use the application of external forces for shaping or roughening the surface. Such methods help in achieving the required surface topography and roughness as well as removing any present surface contamination, which would improve the attachment between the implant surface and the bone [30,31]. Another method for improving the osseointegration of the implant is the selection of an optimum thread profile of the implant [32–34]. Wennerberg et al. concluded that modified implants having a rougher surface compared to smoother machined implants possessed better bone fixation [35]. Souza et al. reviewed the various methods used for nano-scale modification of the titanium implant surface and summarized the various methods. Several methods showed increased roughness values and higher water contact angles, indicating enhanced rate of osseointegration [36] Table 1.

4.2. Acidic treatment

The implant surfaces are treated with acids to remove any oxide scales that may have been formed, thus causing contamination, followed by treating the surface with alkalis to improve the biocompatibility. Takeuchi et al. evaluated the effect of the acids, sodium persulfate ($Na_2S_2O_8$), sulfuric acid (H_2SO_4) and hydrochloric acid (HCl) on the Ti surface. This was followed by rinsing the titanium surface using acetone or ultrapure water [37]. The study concluded that using a blend of 10.0 N hydrochloric acid and acetone reduced the value of Carbon/Titanium and Nitrogen/Titanium to the highest extent among the acids used. Treating the Ti surface with 5.0% sodium persulfate and acetone also gave desirable results, however left behind a residue of $S_2O_8^{2-}$ on the surface. Similar phenomena were observed on Ti surfaces treated with 0.10–10.0 N sulfuric acid. Wen et al. conducted a two-step chemical treatment process by treating the Ti sample using hydrochloric acid and sulfuric acid, followed by boiling in a sodium hydroxide (NaOH) solution [38]. The objective of this process was to enable quick deposition of Calcium Phosphate Layers (CPL) on the surface of commercially available titanium implants to improve the bioactivity and bone bonding capability of the implants. Treating the surface using the acid produced several acid-etched pits and increased the surface area. The alkali treatment that followed formed a microporous surface layer and more titanium oxide was formed in the microporous layer. This significantly improves the adhesion of CPL to the Ti surface. Ban et al. evaluated the consequence of concentrated sulfuric acid on the surface of titanium [39]. In this study, commercially pure Ti was treated with concentrated sulfuric acid (48.0%) to study the changes on the Ti surface. The surface roughness values obtained were higher as compared to those achieved after etching titanium using varying concentrations of other acids. Nanci et al. developed a method to modify the titanium surface to promote the tissue-healing phenomena and improve the implant integration [40]. The titanium surface was first treated using H_2SO_4 and H_2O_2 to clean the surface of the implant and generate a stable TiO_2 layer. An aminoalkylsilane layer was then covalently attached to the TiO_2 layer. This helped in inducing biological activity and promoted the tissue healing process to improve the implant integration with the bone and soft tissues. Thus, acidic treatment is a commonly used method, followed by treating the surface with an alkali to improve biocompatibility.

Table 1
Some of the implant surface treatment methods and corresponding roughness and water contact angles [36].

Grit-blasting	Etching substance	Roughness (μm)	Water contact angle (degrees)
Al_2O_3 (250–300 μm)	18% HCl/48% H_2SO_4	1.66 ± 0.10	117.6
Al_2O_3 (355–425 μm)	HCl/H_2SO_4 (1:3)	2.92 ± 0.22	–
ZrO_2 (250 μm)	98% H_2SO_4/36.50% HCl ($H_2O_2/HCl/H_2SO_4$ (v/v – 2:4:3))	7.63 ± 1.14	131.72 ± 2.07
SiO_2 (250 μm)	$H_2O/HCl/H_2SO_4$ (v/v – 2:4:3)	1.97 ± 0.19	79.08 ± 2.60

4.3. Hydrogen peroxide treatment

Khodaei et al. conducted a study using hydrogen peroxide (H_2O_2) for altering the surface of titanium implants to enhance the bone-bonding ability and increase the osseointegration rate of the implant [12]. In this study, the effect of chloride (Cl) and fluoride (F) ions (oxidizing ions) was observed. The order of the thickness of the anatase (TiO_2) layer was such that the hydrogen peroxide treated sample had the greatest thickness of the anatase layer, followed by the hydrogen peroxide-chloride sample and lastly the hydrogen peroxide-fluoride sample Fig. 2. The presence of anatase (a bioactive phase) on the surface of titanium would make the sample less bio-inert. However, it was observed that titania gel from the titanium surface was mainly dissolved by the fluoride ions and partly by the chloride ions, thus reducing the formation of anatase. According to the wettability measurement, hydrogen peroxide-chloride sample had the highest hydrophilicity and the hydrogen peroxide-fluoride sample had the greatest hydrophobicity. Thus, the hydrogen peroxide-chloride sample had the smallest water contact angle, followed by the hydrogen peroxide sample and lastly by the hydrogen peroxide-fluoride sample. The reduced water contact angle lead to an increase in the wettability, which increased the adsorption of protein, thus leading to improved cell adhesion. Karthega et al. conducted experiments to study the effect of varying concentrations of hydrogen peroxide on titanium [41]. Titanium was treated with H_2O_2 of varying concentrations, 25.0 wt%, 15.0 wt% and 5.0 wt%. Titanium, which was treated using the 15.0 wt% H_2O_2 solution exhibited the highest thickness of the anatase titania layer. The biocompatibility of the samples was tested by immersing the samples in a Simulated Body Fluid (SBF) solution. The order of the ease in which the calcium phosphate layer was formed was 15.0 wt% sample was greater than the 5.0 wt% sample which was in turn greater than the 25.0 wt% sample and all of these samples were greater than the untreated sample. The titanium sample treated with the 15.0 wt% H_2O_2 solution exhibited the highest biocompatibility and bone-bonding aptitude. The electrochemical tests also showed that this sample possessed enhanced corrosion resistance. Janson et al. conducted an experiment and concluded that soaking the titanium surface in a 30 wt% H_2O_2 solution at 80 °C added antibacterial properties while successive treatment with sodium hydroxide and calcium hydroxide solution improved biocompatibility [42].

4.4. Titania/Hydroxyapatite coatings

Wang et al. conducted experiments to study the effect of porous and petaling structured titanium oxide/hydroxyapatite coatings on titanium, prepared by Micro-Arc Oxidation (MAO) [13]. Titanium, being bio-inert, cannot osseointegrate with the human bone. Hydroxyapatite (HA) is one of the principal inorganic constituents of the human bone tissue. Thus, it is coated on the surface of the titanium implant. MAO was chosen over traditional methods of depositing hydroxyapatite such as sol–gel method, ion beam-assisted deposition method [43] and plasma spraying method [44], due to the high bonding strength and stability that is achieved. The voltage and current values were varied during the MAO process to achieve different densities and thicknesses of the porous and petaling layer. The roughness values of the petaling structured surface (0.76–1.06 μm) was higher than the roughness

Please cite this article as: A. Kurup, P. Dhatrak and N. Khasnis, Surface modification techniques of titanium and titanium alloys for biomedical dental applications: A review, Materials Today: Proceedings, https://doi.org/10.1016/j.matpr.2020.06.163

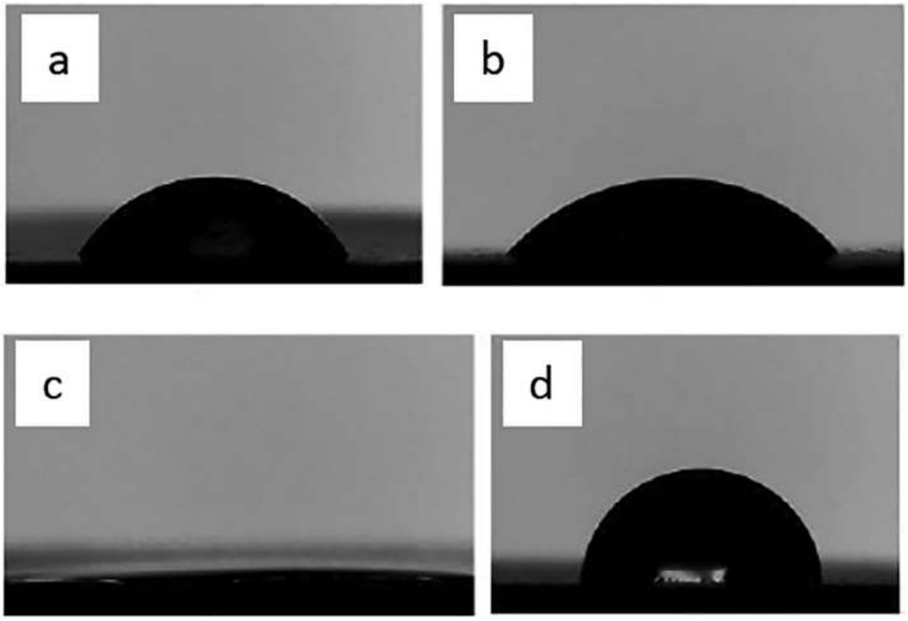

Fig. 2. Water contact angles of (a) Untreated sample (b) H_2O_2 sample (c) H_2O_2 + Cl sample (d) H_2O_2 + F sample [12].

value for porous structured surface (0.33 μm), which in turn was higher than that of the polished surface (0.16 μm). In addition, the water contact angle decreased from about 88° for the polished surface, to about 57° for the porous structured surface and finally about 14° to 0° for the petaling structured Ti surface Fig. 3. Thus, the hydrophilicity of the titanium surface was increased. It was theorized that the increase in the density of hydroxyapatite petals increased the roughness of the implant surface and hydroxyapatite exposed area, which in turn would increase the cell bonding and production. This was confirmed by observing that the promoted the adhesion and proliferation of MC3T3-E1 cells, especially on the petaling structures. It was concluded that the petaling structure proved more useful compared to the traditional porous structure to increase the biocompatibility. Ramires et al. evaluated the biocompatibility of titanium oxide/hydroxyapatite coatings of different ratios (w/w - TiO_2/HA 0.5, TiO_2/HA 1.0, TiO_2/HA 2.0), obtained by sol–gel process [14]. The cytotoxicity test showed that samples obtained by treating with titanium oxide/hydroxyapatite did not affect the cell viability and proliferation. Of these samples, TiO_2/HA 1.0 proved the most beneficial. Thus, it was concluded that the titanium oxide/hydroxyapatite coatings were bioactive, as the surface hydroxyl (OH) groups stimulated the precipitation of calcium (Ca) and phosphate, thus enhancing the interactions with osteoblastic cells.

4.5. Nitride coatings

Brunello et al. studied the biocompatibility and antibacterial activity of four different samples: uncoated titanium alloy (Ti64), anodized and coated with titanium nitride and zirconium nitride [15]. These coatings were applied on the titanium surface using Physical Vapor Deposition (PVD) method. Surface topology analysis revealed that the zirconium nitride coating had the lowest roughness value (0.066 μm), while the titanium nitride (0.116 μm) and anodized (0.112 μm) samples had greater roughness value than the uncoated sample (0.09 μm). The biocompatibility was tested using the Methyl Thiazolyl Tetrazolium (MTT) test, based on the proliferation rate of fibroblasts on the titanium and the samples showed similar results. The Ames test, used to assess the mutagenic potential, showed that none of the samples showed any mutagenic activity. Zirconium nitride, followed by titanium nitride possessed the highest antibacterial activity among the different samples. Hove et al. reviewed the effects of titanium nitride (TiN) coatings on the implant surfaces [16]. It was observed that the titanium nitride coating improved the biocompatibility of the implant surfaces. However, reports of third body wear caused by the delamination of the titanium nitride were also reported. This could be an effect of the coating process, and hence the titanium nitride coating process should be improved and standardized.

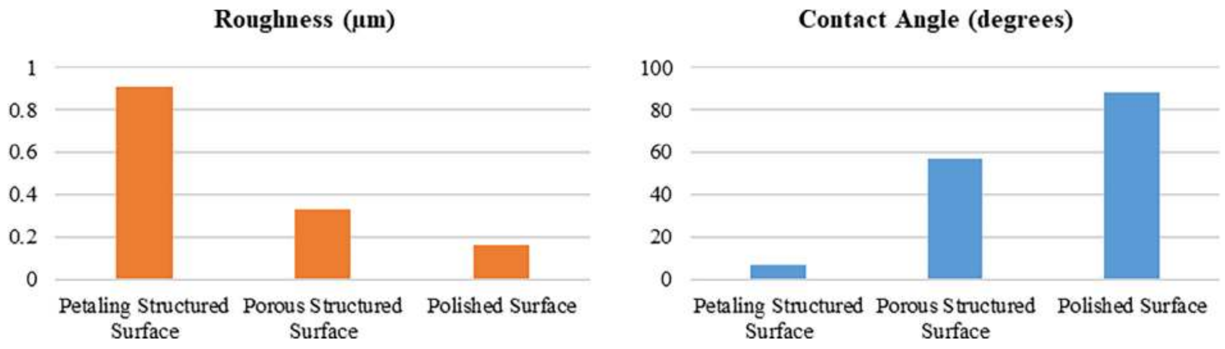

Fig. 3. Roughness and water contact angles of porous and petaling structured titanium oxide/hydroxyapatite coatings on titanium [13].

Please cite this article as: A. Kurup, P. Dhatrak and N. Khasnis, Surface modification techniques of titanium and titanium alloys for biomedical dental applications: A review, Materials Today: Proceedings, https://doi.org/10.1016/j.matpr.2020.06.163

4.6. Metal oxide coatings

Trino et al. studied the effects of zinc oxide (ZnO) on the surface of titanium implants [17]. Zinc oxide was chosen as it has high corrosion resistance, high biocompatibility and significant antibacterial activity. The sol–gel technique was chosen over other physical and chemical methods for depositing the zinc oxide film, as it allows a low-cost mass production and excellent substrate adhesion. Another advantage is that zinc oxide films have hydroxyl groups on their surface that can be functionalized by carboxylic acids, esters and acid chlorides, which can result in a more biocompatible and corrosion resistant surface. The zinc oxide films were functionalized with 3-(4-aminophenyl) propionic acid (APPA), polyethylene glycol (PEG), 3-mercaptopropionic acid (MPA) and (3-aminopropyl) trimetoxysilane (APTMS) bio-functional molecules. These samples showed increased corrosion resistance. Of these, zinc oxide functionalized with APPA showed the best results for biocompatibility and corrosion resistance. Sollazzo et al. studied the effects of zirconium oxide (ZrO_2) on the titanium implant surface [18]. Zirconium oxide was selected as it has good chemical stability and great mechanical properties, wear resistance and biocompatibility. The study demonstrated that implants coated with zirconium oxide showed a significantly higher bone-implant contact percentage as compared to untreated samples. This signified that zirconium oxide coatings could improve implant osseointegration. He et al. studied the biological and morphological properties of titanium oxide (TiO_2)/copper oxide (CuO) coatings on titanium [19]. Copper was chosen as it is beneficial for bone formation, has good antibacterial properties and studies have shown that traces of copper enhance the proliferation of osteoblastic cells. The copper coating was first deposited on titanium by pulsed direct current magnetron sputtering, and then annealed to obtain copper oxide doped titanium oxide coatings. Tests revealed that the TiO_2/CuO coatings had high biocompatibility, improved cell proliferation, better corrosion resistance and antibacterial property Table 1.

4.7. Silver (Ag) coatings

Kim et al. studied the effects of a stabilized Ag nanostructure on the surface of a titanium implant [20]. Silver was selected due to its superior biocompatibility and antibacterial activity, as silver ions can penetrate bacteria without damaging the essential cell membranes. The Target-ion Induced Plasma Sputtering (TIPS) method was used to generate the nanostructured layer of silver on titanium. TIPS generated a superior coating on titanium, which had superior mechanical stability and enhanced cell attachment, proliferation and differentiation. The duration of silver coating process on TIPS - titanium was changed (10.0 s, 30.0 s and 120.0 s) and the different samples were compared. The contact angle for TIPS-Ti reduced from about 60° for the unpolished sample to about 5°. This indicated that the TIPS - titanium had superior bioactivity and biocompatibility. However, the contact angle increased with increased silver sputtering time. It was observed that the 10.0 Ag-TIPS-titanium specimens had optimum conditions for cytotoxicity and antimicrobial activity. Excessive concentrations of silver (120.0 Ag-TIPS-titanium) resulted in pro-inflammatory mechanisms and affected the degree of proliferation. Thus, it was concluded that the stabilized silver on a TIPS-titanium surface improved overall healing and provided lasting stability of the implant. Huang et al. studied the outcome of tantalum nitride - silver coatings with varying silver contents on the surface of a titanium implant [21]. Tantalum nitride (TaN), owing to its excellent biocompatibility, was chosen to be doped with silver for an increased antibacterial effect. The tantalum nitride – silver (TaN-Ag) nanocomposite coating with varying silver concentrations was produced using the twin-gun reactive magnetron sputtering process. The various samples tested were tantalum nitride (TaN), TaN-Ag (14.90%), TaN-Ag (17.50%) and TaN-Ag (21.40%). The tantalum nitride coating with 14.90% silver had the highest roughness and elastic modulus values, followed by the tantalum nitride coating, and then by the tantalum nitride coating with 17.50% silver and lastly by the coating with 21.40% silver. The contact angle decreased with the presence of silver particles, and was lower for the TaN-Ag samples than for the tantalum nitride sample. The tantalum nitride coating with 21.40% silver had the least fluorescence concentration and thus retained the smallest amount of bacteria Fig. 4. Thus, it was concluded that the tantalum nitride – silver film improved the antibacterial activity and biocompatibility properties of the implants.

Table 2
Summary of metal oxide coatings on titanium surface.

Author	Coating	Remarks
Trino et al. [17]	ZnO	Increased corrosion resistance Increased interaction of the surface with biomolecules, improving biocompatibility ZnO functionalized with APPA showed best results
Sollazo et al. [18]	ZrO_2	Increased bone-implant contact percentage Enhanced implant osseointegration No toxic and carcinogenic effects observed
He at al. [19]	CuO	Increased biocompatibility and cell proliferation. Increased corrosion resistance and antibacterial property.

4.8. Physical methods

The physical methods include thermal spraying, sputtering and ion deposition [23]. In these processes, there are no chemical reactions that take place. In thermal spraying, the materials are converted into molten liquid droplets at high temperatures and then coated on a base material. Thermal spraying can be further classified as flame and plasma spraying. The temperatures achieved using plasma spraying is much higher than that achieved by flame spraying. Atmospheric Plasma Spraying (APS) and Vacuum Plasma Spraying (VPS) are two forms of plasma spraying. Sputtering is commonly used method to deposit a thin film for ceramic materials and refractory metals, as it is difficult to deposit a coating on these materials using traditional evaporation methods. Sputtering is used to increase the biocompatibility and corrosion resistance of the implants. Recent advances in sputtering include Ion Bean Sputtering (IBS) and Magnetron Sputtering [30].

4.9. Improvement in antibacterial properties

A major reason for implant failure is due to microbial infections caused by the implant. Biofilm formation is the main cause of infections as it is starts immediately after bacterial adhesion. Once the biofilm is formed on the implant, bacterial eradication becomes extremely difficult. Thus, in order to ensure long-term success of the implant, antibacterial properties of the implant plays a major role. Chouirfa et al. have studied the antibacterial properties imparted to the implants by various surface modification techniques [45]. In this respect, Ti nano-coated surfaces have shown a greater effectiveness against bacteria like Streptococcus Mutans, Staphylococcus Aureus and Streptococcus Sanguinis. Similarly, the other techniques explained above such as silver (Ag) coatings, fluoride (F) and chloride (Cl) implanted coatings, titanium nitride (TiN) coatings, hydroxyapatite coatings and TiO_2 have all displayed high antibacterial properties. Smeets et al. have studied the effects of surface modification methods like micro and nano scale modification enhance the rate of osseointegration while inhibiting bacterial adhesion [46]. However, further research is required as the

Please cite this article as: A. Kurup, P. Dhatrak and N. Khasnis, Surface modification techniques of titanium and titanium alloys for biomedical dental applications: A review, Materials Today: Proceedings, https://doi.org/10.1016/j.matpr.2020.06.163

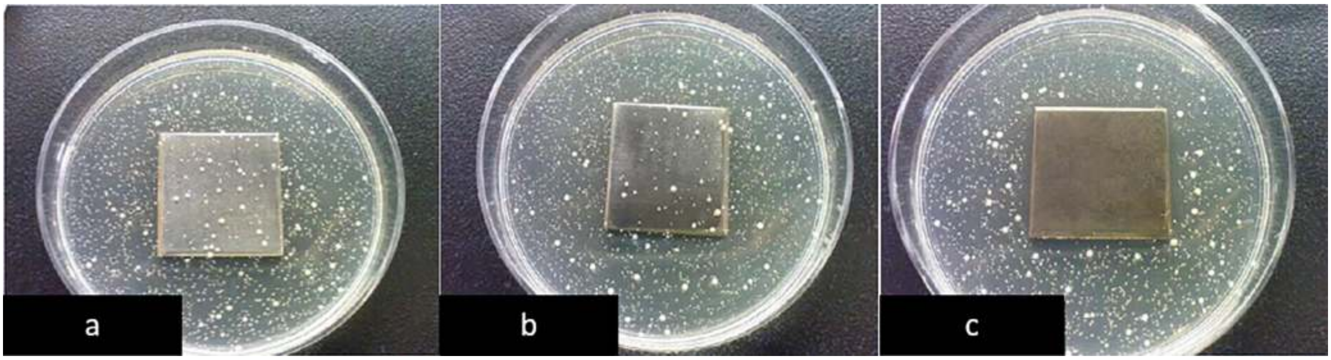

Fig. 4. Bacterial (*S. aureus*) growth on (a) Uncoated titanium sample (b) TaN coated sample (c) TaN with 21.40% silver coated sample [21].

current tests have been mainly in vitro testing and subsequent in vivo testing would be required

5. Limitations and future scope of Ti surface modification techniques

Ti implants are expensive and thus research is being conducted to find suitable substitutes to be used as implant materials. Stainless Steel (SS) 316L has superior corrosion resistance however has poor surface hardness. Thus, research is being conducted to improve the properties of the SS implants by coating with materials like Titanium Nitride (TiN) [47] and Tungsten Carbide (WC) [48]. These methods have demonstrated improved values of wear resistance and hardness, thus improving the properties of the base (SS 316L) metal. Magnesium is another metal that is gaining popularity as a biomedical material. However, its usage has been limited due to its quick degradation. Thus, subsequent research is being conducted to improve the properties of such Mg implants [49]. The use of polymer materials has increased greatly due to several advantages that they possess over metallic biomaterials, such as ability to be easily manufactured into desired size and shape, high protein binding property and biodegradability [1]. Saravanan et al. have studied the wear behaviour of Ultra High Molecular Weight Poly Ethylene (UHMWPE) reinforced with ceramic materials to test their suitability as biomaterials, especially as orthopaedic implants [50].

Some of the other challenges faced by traditional methods of surface coatings like hydroxyapatite coatings is their poor adherence to the titanium surface. This could increase the usage of nanoparticle coatings on the implant surface. Nanoparticles of silver (Ag), Zinc oxide (ZnO), Copper oxide (CuO), titanium nanotubes, nanocrystalline diamond particles and graphene show tremendous potential. Such methods possess improved osteoconductive and antimicrobial properties. Another prospective study could be into multifunctional coatings that would combine the properties of two different coating methods. For instance, titanium implants with a combined HA and graphene coating provides the biological advantages of the HA coating, while graphene is used to strengthen the brittle nature of the HA coating [1].

Thus, nanoparticle and multifunctional coatings show tremendous potential.

6. Conclusion

Some of the most promising surface modification techniques of Ti and its alloys for biomedical uses have been reviewed. In recent times, there has been an increased development of biomaterials that possess the ability to be implanted into the human body. These include applications like dental implant, orthopaedic implants and cardiovascular implants. Such materials are usually metals, polymers and ceramics. Presently, metals are the most frequently used as implant biomaterials as they combine significant mechanical strength along with a great potential to be biocompatible.

The popularity of titanium dental implants is on the rise and with this, the need to produce implants with superior life and success rate is necessary. However, titanium remains relatively unchanged in the human body, making it biologically inert. Therefore, in order to make the titanium implant biocompatible, it is necessary to alter the implant surface to increase the rate of osseointegration and to provide it with a greater abrasion resistance. The methods that have been reviewed in this paper have all shown major improvement in the biocompatibility, antibacterial activity, and anti-corrosion property of the Ti implants. These experiments are a good indicator that modifying the surface of the titanium implant would improve the stability and performance of the implants. The future of surface modification techniques would be to develop nanoparticle and multifunctional coatings that would combine the advantages of various coatings and provide a more favourable method of surface modification.

The popularity and usage of Ti implants is increasing each year. These implants are in constant contact with the human cells, thus, the interaction between the implant surface and the human cell should be studied and understood even further. This knowledge will be key in developing new implants that would overcome the existing flaws. It has been proven that surface modification has tremendous potential to improve the performance of the Ti implant, thus further research is necessary to develop novel surface modification techniques that will produce an implant which will have superior biocompatibility, antibacterial property, and corrosion and wear resistance.

CRediT authorship contribution statement

Alekh Kurup: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Project administration, Software, Validation, Visualization, Writing - original draft. **Pankaj Dhatrak:** Data curation, Formal analysis, Investigation, Project administration, Software, Supervision, Validation, Visualization, Writing - review & editing. **Neha Khasnis:** Data curation, Formal analysis, Investigation, Methodology, Validation, Visualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Please cite this article as: A. Kurup, P. Dhatrak and N. Khasnis, Surface modification techniques of titanium and titanium alloys for biomedical dental applications: A review, Materials Today: Proceedings, https://doi.org/10.1016/j.matpr.2020.06.163

Acknowledgements

The author(s) received no financial support for the research, authorship, and/or publication of this article.

References

[1] Fahimeh Sadat Tabatabaei, Regine Torres, Lobat Tayebi, Biomedical materials in dentistry, Applications of Biomedical Engineering in Dentistry, Springer, 2020.

[2] Manmeet Kaur, K. Singh, Review on titanium and titanium based alloys as biomaterials for orthopaedic applications, Mater. Sci. Eng., C 102 (2019) 844–862.

[3] Karthika Prasad, Olha Bazaka, Ming Chua, Madison Rochford, Liam Fedrick, Jordan Spoor, Richard Symes, Marcus Tieppo, Cameron Collins, Alex Cao, David Markwell, Kostya (Ken) Ostrikov, Kateryna Bazaka, Metallic biomaterials: current challenges and opportunities, Materials 10 (2017) 884.

[4] Divya Zindani, J. Kaushik Kumar, Paulo Davim, Metallic biomaterials—a review, Mech. Behav. Biomater. (2019).

[5] Mitsuo Niinomi, Design and development of metallic biomaterials with biological and mechanical biocompatibility, J. Biomed. Mater. Res. (2019).

[6] Mona Alizadeh-Osgouei, Yuncang Li, Cuie Wen, A comprehensive review of biodegradable synthetic polymer-ceramic composites and their manufacture for biomedical applications, Bioact. Mater. 4 (2019) 22–36.

[7] Rajan Choudhary, Mohit Saraswat, Senthil Kumar Venkatraman, A fundamental approach toward polymers and polymer composites: current trends for biomedical applications, Polym. Nanocompos. Biomed. Eng. 2019.

[8] Monika Golda-Cepa, Klas Engvall, Minna Hakkarainen, Andrzej Ko, Recent progress on parylene C polymer for biomedical applications: a review, Prog. Org. Coat. 140 (2020) 105493.

[9] Gurbinder Kaur, Vishal Kumar, Francesco Baino, John C. Mauro, Gary Pickrell, Iain Evans, Oana Bretcanu, Mechanical properties of bioactive glasses, ceramics, glass-ceramics and composites: state-of-the-art review and future challenges, Mater. Sci. Eng., C 104 (2019) 109895.

[10] Marcela Arango-Ospina, Fangtong Xie, Isabel Gonzalo-Juan, Ralf Riedel, Emanuel Ionescu, Aldo R. Boccaccini, Review: silicon oxycarbide based materials for biomedical applications, Appl. Mater. Today 2019.

[11] Mukta Kulkarni, Anca Mazare, Patrik Schmuki, Ales Iglic, Biomaterial surface modification of titanium and titanium alloys for medical applications, in: Alexander Seifalian et al. (Eds.), Nanomedicine, One Central Press (OCP), 2014.

[12] Mohammad Khodaei, Hossein Saleh Kelishadi, The effect of different oxidizing ions on hydrogen peroxide treatment of titanium dental implant, Surf. Coat. Technol. (2018).

[13] Xiaolin Wang, Baoe Li, Linxi Zhou, Jianwei Ma, Xianlin Zhang, Haipeng Li, Chunyong Liang, Shimin Liu, Hongshui Wang, Influence of surface structures on biocompatibility of TiO2/HA coatings prepared by MAO, Mater. Chem. Phys. (2018).

[14] P.A. Ramires, A. Romito, F. Cosentino, E. Milella, The influence of titania/hydroxyapatite composite coatings on in vitro osteoblasts behaviour, Biomaterials 22 (2001) 1467–1474.

[15] G. Brunello, P. Brun, C. Gardin, L. Ferroni, E. Bressan, R. Meneghello, et al., Biocompatibility and antibacterial properties of zirconium nitride coating on titanium abutments: an in vitro study, PLoS ONE 13 (6) (2018) e0199591.

[16] Ruud P. van Hove, Inger N. Sierevelt, Barend J. van Royen, Peter A. Nolte, Titanium-nitride coating of orthopaedic implants: a review of the literature, BioMed Res. Int. 2015.

[17] Luciana D. Trino, Leonardo F.G. Dias, Luiz G.S. Albano, Erika S. Bronze-Uhle, Elidiane C. Rangel, Carlos F.O. Graeff, Paulo N. Lisboa-Filho, Zinc oxide surface functionalization and related effects on corrosion resistance of titanium implants, Ceram. Int. 44 (2018) 4000–4008.

[18] Vincenzo Sollazzo, Furio Pezzetti, Antonio Scarano, Adriano Piattelli, Carlo Alberto Bignozzi, Leo Massari, Giorgio Brunelli, Francesco Carinci, Zirconium oxide coating improves implant osseointegration in vivo, Dental Mater. 24 (2008) 357–361.

[19] Xiaojing He, Guannan Zhang, Xin Wang, Ruiqiang Hang, Xiaobo Huang, Lin Qin, Bin Tang, Xiangyu Zhang, Biocompatibility, corrosion resistance and antibacterial activity of TiO2/CuO coating on titanium, Ceram. Int. (2017).

[20] Sungwon Kim, Cheonil Park, Kwang-Hee Cheon, Hyun-Do Jung, Juha Song, Hyoun-Ee Kim, Tae-Sik Jang, Antibacterial and bioactive properties of stabilized silver on titanium with a nanostructured surface for dental applications, Appl. Surf. Sci. (2018).

[21] Heng-Li Huang, Yin-Yu Chang, Meng-Cheng Lai, Cai-Rong Lin, Chih-Ho Lai, Tzong-Ming Shieh, Antibacterial TaN-Ag coatings on titanium dental implants, Surf. Coat. Technol. 205 (2010) 1636–1641.

[22] Introduction to implant dentistry: a student guide, J. Oral Maxillofacial Surg. 75(Supplement 2) (February 2017).

[23] S. Anil, P.S. Anand, H. Alghamdi, J.A. Jansen, Dental implant surface enhancement and osseointegration, in: Ilser Turkyilmaz (Ed.), Implant Dentistry - A Rapidly Evolving Practice, InTech, 2011.

[24] H. Terheyden, N.P. Lang, S. Bierbaum, B. Stadlinger, Osseointegration – communication of cells, Clin. Oral Impl. Res. 00 (2011) 1–9, https://doi.org/10.1111/j.1600-0501.2011.02327.x.

[25] María B. Guglielmotti, Daniel G. Olmedo, Rómulo L. Cabrini, Research on implants and osseointegration, Periodontology 2000 (2019).

[26] Y. Sasikumar, K. Indira, N. Rajendran, Surface modification methods for titanium and its alloys and their corrosion behaviour in biological environment: a review, J. Bio- Tribo-Corros. 5 (2019) 36.

[27] Sauro Grassi, Adriano Piattelli, Luciene Cristina de Figueiredo, Magda Feres, Leandro de Melo, Giovanna Iezzi, Rodolfo Candia Alba Jr., Jamil Awad Shibli, Histologic evaluation of early human bone response to different implant surfaces, J. Periodontol. (2006).

[28] T. Hanawa, Transition of surface modification of titanium for medical and dental use, Titanium Med. Dental Applications (2018).

[29] Pankaj Dhatrak, Uddhav Shirsat, Vijay Deshmukh, Fatigue life prediction of commercial dental implants based on biomechanical parameters: a review, J. Mater. Sci. Surf. Eng. 3 (2) (2015) 221–226.

[30] Xuanyong Liu, Paul K. Chu, Chuanxian Ding, Surface modification of titanium, titanium alloys, and related materials for biomedical applications, Mater. Sci. Eng. R 47 (2004) 49–121.

[31] Pietro Mandracci, Federico Mussano, Paola Rivolo, Stefano Carossa, Surface treatments and functional coatings for biocompatibility improvement and bacterial adhesion reduction in dental implantology, Coatings (2016).

[32] Pankaj Dhatrak, Uddhav Shirsat, S. Sumanth, Vijay Deshmukh, Finite element analysis and experimental investigations on stress distribution of dental implants around implant-bone interface, Mater. Today:. Proc. 5 (2018) 5641–5648.

[33] Pankaj Dhatrak, Vedant Girme, Uddhav Shirsat, S. Sumanth, Vijay Deshmukh, Significance of orthotropic material models to predict stress around bone-implant interface using numerical simulation, BioNanoScience (2019).

[34] P. Dhatrak, U. Shirsat, V. Deshmukh, S. Sumanth, Fatigue life prediction of commercial dental implant using analytical approach and verification by FEA, in: S. Seetharamu, K. Rao, R. Khare (Eds.), Proceedings of Fatigue, Durability and Fracture Mechanics. Lecture Notes in Mechanical Engineering, Springer, Singapore, 2018.

[35] Ann Wennerberg, Tomas Albrektsson, Carina Johansson, Bijrje Andersson, Experimental study of turned and grit-blasted screw-shaped implants with special emphasis on effects of blasting material and surface topography, Biomaterials 17(1) 1996.

[36] Julio C.M. Souza, Mariane B. Sordi, Miya Kanazawa, Sriram Ravindran, Bruno Henriques, Filipe S. Silva, Conrado Aparicio, Lyndon F. Cooper, Nano-scale modification of titanium implant surfaces to enhance osseointegration, Acta Biomater. 94 (2019) 112–131.

[37] M. Takeuchi, Y. Abe, Y. Yoshida, Y. Nakayama, M. Okazaki, Y. Akagawa, Acid pretreatment of titanium implants, Biomaterials 24 (2003) 1821–1827.

[38] H.B. Wen, Q. Liu, J.R. De Wijn, K. De Groot, Preparation of bioactive microporous titanium surface by a new two-step chemical treatment, J. Mater. Sci. - Mater. Med. 9 (1998) 121–128.

[39] Seiji Ban, Yukari Iwaya, Hiroshi Kono, Hideo Sato, Surface modification of titanium by etching in concentrated sulphuric acid, Dent. Mater. 22 (2006) 1115–1120.

[40] A. Nanci, J.D. Wuest, L. Peru, P. Brunet, V. Sharma, S. Zalzal, M.D. McKee, Chemical modification of titanium surfaces for covalent attachment of biological molecules, Protein Coupling Titanium (1997).

[41] M. Karthega, S. Nagarajan, N. Rajendran, In vitro studies of hydrogen peroxide treated titanium for biomedical applications, Electrochim. Acta (2009).

[42] Oscar Janson, Satwik Gururaj, Shiuli Pujari-Palmer, Marjam Karlsson Ott, Maria Strømme, Håkan Engqvist, Ken Welch, Titanium surface modification to enhance antibacterial and bioactive properties while retaining biocompatibility, Mater. Sci. Eng., C 96 (2019) 272–279.

[43] F.Z. Cui, Z.S. Luo, Q.L. Feng, Highly adhesive hydroxyapatite coatings on titanium alloy formed by ion beam assisted deposition, J. Mater. Sci. - Mater. Med. 8 (1997) 403–405.

[44] K. de Groot, R. Geesink, C.P.A.T. Klein, P. Serekian, Plasma sprayed coatings of hydroxylapatite, J. Biomed. Mater. Res. 21 (1987) 1375–1381.

[45] H. Chouirfa, H. Bouloussa, V. Migonney, C. Falentin-Daudré, Review of titanium surface modification techniques and coatings for antibacterial applications, Acta Biomater. (2018), https://doi.org/10.1016/j.actbio.2018.10.036.

[46] Ralf Smeets, Bernd Stadlinger, Frank Schwarz, Benedicta Beck-Broichsitter, Ole Jung, Clarissa Precht, Frank Kloss, Alexander Gröbe, Max Heiland, Tobias Ebker, Impact of dental implant surface modifications on osseointegration, BioMed Res. Int. (2016), Article ID 6285620.

[47] I. Saravanan, A. Elaya Perumal, R. Franklin Issac, S.C. Vettivel, A. Devaraju, Optimization of wear parameters and their relative effects on TiN coated surface against Ti6Al4V alloy, (2015), doi: 10.1016/j.matdes.2015.11.119

[48] M. Saravanan, N. Venkateshwaran, A. Devaraju, A. Krishnakumari, Tribological behavior of thin nano tungsten carbide film deposited on 316l stainless steel surface, Surf. Rev. Lett. (2017) 1950027.

[49] K. Rajkumar, K. Ramraji, G. Namratha, S. Manoj, A. Gnanavelbabu, A study of bio and tribo modifier on degradation of magnesium-calcium carbonate biomaterial, Mater. Today:. Proc. (2019).

[50] I. Saravanan, A. Devaraju, Wear mechanism of UHMWPE polymer composites for bio medical applications, Mater. Res. Express 6 (2019) 105355.

Please cite this article as: A. Kurup, P. Dhatrak and N. Khasnis, Surface modification techniques of titanium and titanium alloys for biomedical dental applications: A review, Materials Today: Proceedings, https://doi.org/10.1016/j.matpr.2020.06.163