Coatings for dental applications

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Abstract

Dental implants have become a reliable treatment option in oral rehabilitation of partially or fully edentulous patients to secure various kinds of prostheses. Established standard procedures exist for tooth replacement in various zones with varying degrees of success and challenges. Overall, the long-term success of dental implants largely depends on their surface characteristics and osseointegration. Although, the success rate of dental implants is high in comparison to orthopaedic implants, insufficient integration, local tissue inflammation, and infection are still persistent issues. Accordingly, various types of biomaterial coatings using a range of techniques are commonly used to improve the overall performance of dental implants and to overcome some of the persistent issues. The function of the implant coated material includes enhancing the cellular changes which in turn accelerate the healing process through improved osseointegration and antibacterial properties. Consequently, coatings for dental applications are gaining significant attention and interest among researchers across the globe. This paper, therefore, aims to introduce coating materials and associated techniques used in the context of dental application for improved biocompatibility and biofunctionality.

Keywords: Dental; coating techniques; Hydroxyapatite; biocompatibility; antibacterial; implants.

1. Introduction

A dental implant is a medical device used to restore or replace damaged or missing teeth. The role of the dental implant is to re-establish chewing and enhances appearance [1]. A regular dental implant is composed of three-component as shown in Fig. 1. These are the implant fixture, commonly referred to as post or pin, the abutment that is attached to the implant fixture, and the prosthesis or dental reconstruction that may be a crown, bridge, or denture [2]. A key criterion for dental implant material is their biocompatibility, bio-functionality, and the potential for osteointegration. A dental implant biomaterial should also be able to provide good biomechanical interaction between the implant and jaw bone [3][4]. These implant materials should also be cost-effective with a long shelf-life [5].

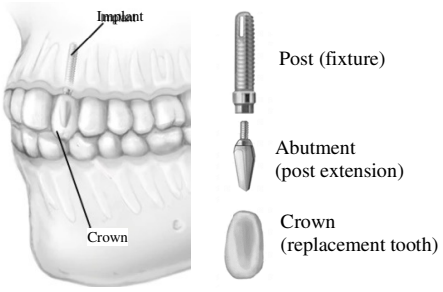

Fig. 1. Components of the restored dental implant, adapted from [6].

Metallic materials have long been used as potential biomaterials for dentistry. Besides, metal-free treatments have also become popular in dentistry from the esthetic viewpoint. On the other hand, abrupt technological evolution on ceramics and polymers make it possible to apply these materials to medical devices in the last three decades [7]. Commonly used biomaterials for dental implants include Stainless Steel, Titanium (Ti) and alloys, and Cobalt-Chromium (Co-Cr), Aluminum oxide, Zirconium oxide, Titanium oxide, Calcium phosphate ceramics, Glass-ceramics, Biopolymers [8], [9]. Among these, titanium and its alloys are largely considered ideal due to the superior biocompatibility [10], high strength to weight ratio, corrosion resistance, chemical stability, low modulus of elasticity, and manufacturing feasibility [11], [12]. Studies have extensively investigated the potential impact of the titanium implant surface on the biological response as well as the effect of the surface characteristics [13]. When titanium is exposed to air, water, or other electrolytes, a thin layer of titanium oxide is formed on the surface [14], [15]. This oxide layer makes titanium an excellent biomaterial that can be characterised by the adsorption of various biomolecules as well as subsequent attachment and spread of cells as shown in Fig. 2.

However, titanium or other dental implant material suffers from a variety of complications and rarely provides a comparable function to native physiological structures. Dental implants are restricted to their function due to complicating factors such as insufficient integration in the host bony tissue, inflammatory reactions, and infection, problems on the surface of the device, and direct biological environments. Studies show that micro displacements below 50 to 125 µm do not interfere with bone repair and lead to gradual osseointegration in pure titanium and titanium alloy implants [16], [17].

Failure of dental implants is primarily caused by two types: biological (Fig. 3) and technological (fracturing, lack of retention, loosening of the screws) [18]. The stability of the dental implant is accomplished through osseointegration. Proper interaction between the head of the implant and the gingiva, known as biosealing, is achieved to maintain a barrier mechanism. However, the absence of biosealing can lead to the infiltration of bacteria into the peri-implant pocket and subsequently to the

formation of dental plaque. Inflammation of the soft tissue surrounding the implant (mucositis) and infection of the supporting bone (periimplantitis) is caused by plaque formation unless treated [19].

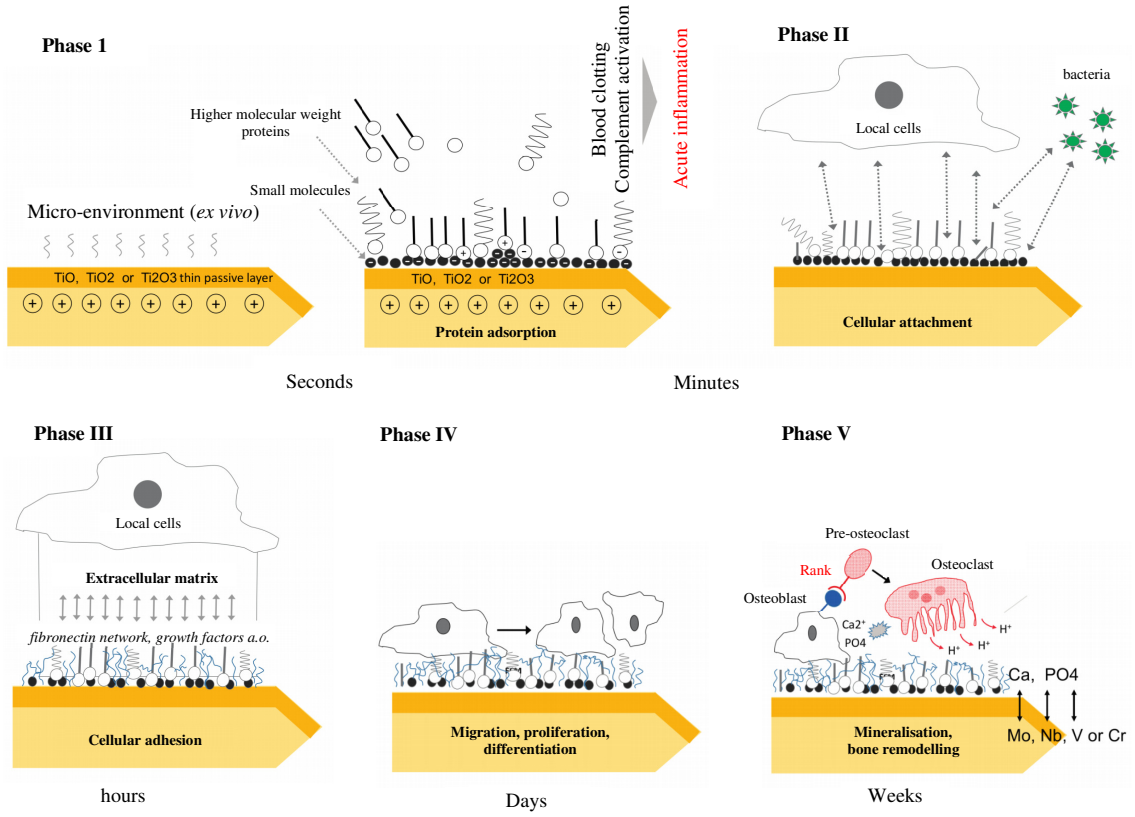

Fig. 2. Phases of the reaction of titanium implant with its *in vivo* environment [14].

Applying suitable surface-responsive materials to the dental implants is therefore essential. These surface reactive materials bind well with the living tissues through physical or chemical reactions which allow the implants to be bio-actively joined. There is therefore considerable motivation to change the surface characteristics to control the biological reaction and improve the functionality of the system [20]. As a result, surface engineering becomes critical for long-term implantation efficiency, improving dental implant performance and overcoming its bio-inert nature along with other disadvantages (e.g. low fretting fatigue resistance and low tribological properties) [21][22][23]. Thus, a huge effort has been put into providing an ultimate solution to all these limitations by industry and research institutions.

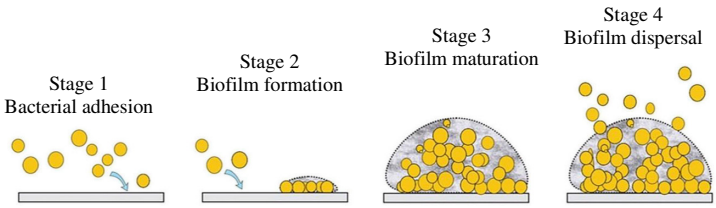

Fig. 3. Biofilm formation stages in a dental implant [19][24].

The area of coating for dental application is one of the actively investigated topics. While the initial efforts on the development of coatings for dental application begun a few decades ago, research is being carried out around the world as shown in Fig. 4a. The major contribution is from United States (26%)

followed by China (16%) and Japan (10%) (Fig. 4b). This study aims to bring forward the types of dental implant coating materials and associated techniques that are being investigated around the world to enable functional decision making.

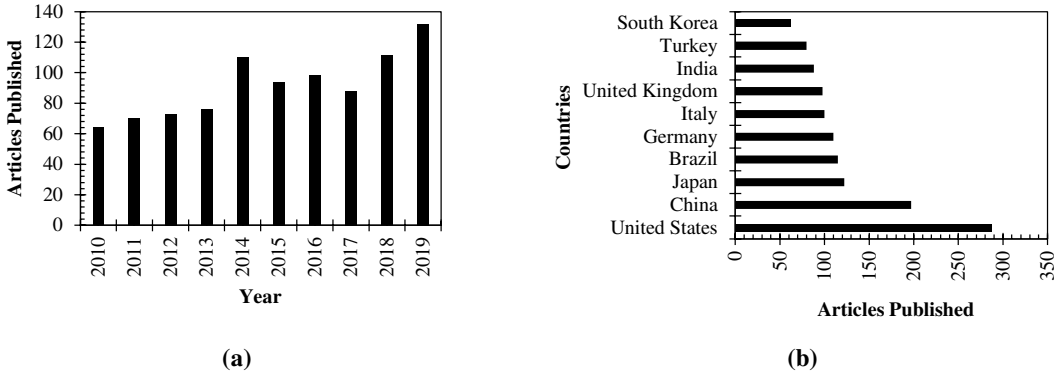

Fig. 4. Number of Scopus indexed publications on coatings for dental applications from (a) 2010-2019 and (b) countries that lead in contribution.

2. Coating techniques for dental applications

Several materials were used on dental implants as coatings. These materials include carbon, bisphosphonates, bioactive glass, bioactive ceramics, fluoride, hydroxyapatite (HA), calcium phosphate, calcium silicate, and titanium nitride (TiN) [5]. Cu, Ag, and Cu-Ag particles are also incorporated with the coating materials to improve the antibacterial activity [25]–[28]. Surface coatings on dental implants can lead to uniform bone regeneration and integrity between the implant surface and bone tissue. The coating materials are deposited on the dental implants using several techniques [29] which are detailed in subsequent sections.

2.1.Plasma spraying

Plasma spraying consists of spraying a coating material by using an ionized gas or gas mixture. Usually, a combination of Ar or N_2-based inert gases with H_2 and He additions are used. Electrical fields are used to ionise the gases and to produce thermal plasmas or plasma arcs that are used to move the material from the feedstock to the surface of the substrate. The schematic of a plasma torch is presented in Fig. 5. Atmospheric plasma spraying is a conventional thermal spray process that has been widely used for biofunctionalised coating deposition. The production of coatings with fine microstructures (sub-micrometer/nanometer-scale) has been developed since the mid-1990s. These coatings improved their physical and mechanical properties, such as surface area, solubility, and many others. For plasma spraying, the coatings have a characteristic lamellar structure due to successive impingement of splats, which also results in micro-defects such as unmelted particles, gas pores, and weak interconnection between splats that could deteriorate the coating performance.

Depending on the configuration of the nozzle and operating parameters, the temperature of the plasma jet varies from 8000-14000 °C at the exit of the nozzle (on the jet axis) and gas velocity from 200 - 600 m/s [30][31]. The plasma torch is produced using copper or graphite anode and thoriated tungsten cathode. The discharge of the electric arc produced between the anode and the cathode ionizes the gas (or gas mixture) that expands into the jet-forming atmosphere.

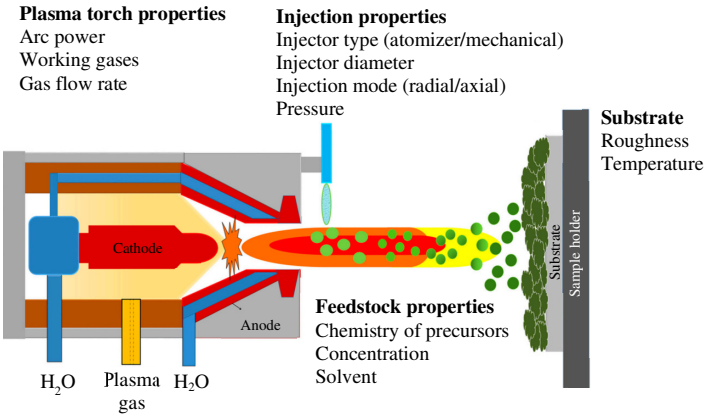

Fig. 5. Schematic of the plasma spray torch, adapted from [31], [32].

The coating material (powder) is introduced into the jet, accelerated, and propelled to the implant substrate [33]. Hydroxyapatite based coatings were developed using plasma spraying by different researchers [34][35][36]. The addition of ZnO, SiO_2, and Ag_2O in HA coating on the mechanical and biological properties was investigated by Vu et al. [34]. HA coating with dopant exhibited enhanced in vivo osseointegration through an early onset bone maturation process (Fig. 6 (a)). The highest total bone formation (Fig. 6 (b) and (c)) was observed for ZnSiAg-HA coating. Karamian et al. [36] assessed the bioactivity of plasma-sprayed hydroxyapatite/zircon nano biocomposites coating on 316L stainless steel dental implant in simulated body fluid (SBF) and achieved nanostructure with a mean crystallite size of 30–40 nm in diameter. The coatings were deposited with good bond strength and osseointegration between the implant and host tissue using the plasma spray system. The plasma-sprayed yttria-stabilised zirconia polycrystal (YZP) coating reinforced titania (TiO_2) shows good mechanical properties and bioactivity [37].

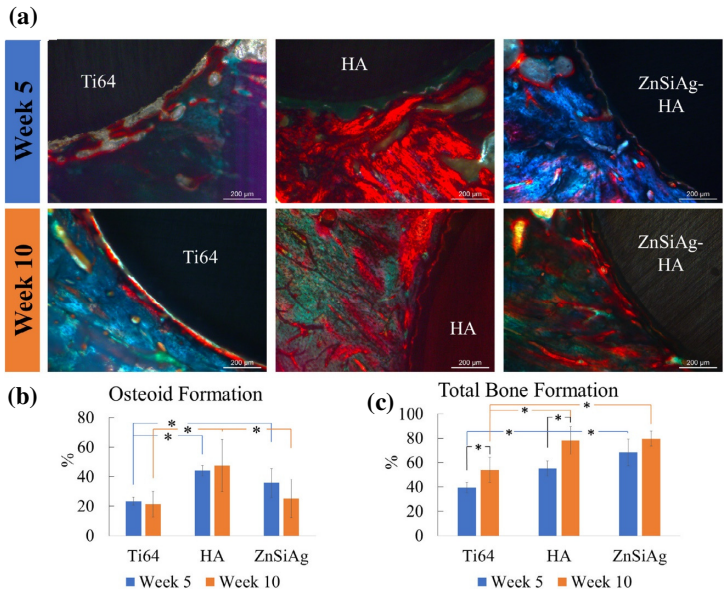

Fig. 6. (a) Optical microscopy images showing osteoid formation for pure Ti64, HA-coated Ti64, and ZnSiAg-HA coated Ti64 (b) Total osteoid formation and (c) Total bone formation in % around the implant [38].

2.2.High Velocity Oxy Fuel spraying (HVOF)

This combustion technique combines oxygen and fuel to produce heat and high particle speeds to achieve dense coatings with increased bond strength. This technology has a relatively lower flame temperature than in the standard spray process, resulting in greater adherence and density. HVOF spraying is a promising technique due to its low flame temperature (less than 3000 K) and high particle velocity (500-1000 m/s) to produce coatings with low porosity, high density, low oxidation level, high hardness, and higher bond strength and also because of its flexibility and cost-effectiveness [30][39][40].

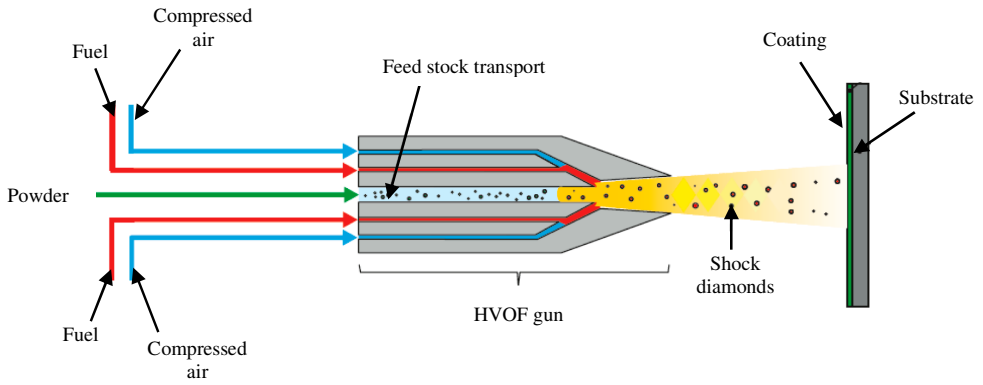

Fig. 7. Scheme of high velocity oxy-fuel spraying [41].

The microstructure and the physical characteristics of the HVOF coating depend on the physical and chemical properties of the particle impinging on the substrate, which in turn depends on several parameters such as the design of the gun, the fuel/oxygen ratio, the position of the substrate relative to the gun, the size, and shape of the particle and injection [42]. Fig. 7 depicts the schematic representation HVOF spraying system.

Haman et al. [43] used the HVOF method to deposit HA and fluorapatite coatings on the titanium substrate. Nano HA powder was used to develop HVOF sprayed coatings [44] and the resulted coatings were an amorphous and crystalline phase mixture. The hardness value was 2.15 ± 0.08 GPa. HA coatings interacted strongly with the SBF and exhibited a highly osteoconductive nature and have the potential for prosthetic implant applications.

2.3.Pulsed laser deposition coating technique

The material to be coated in the vacuum chamber is strike with a high-power pulsed laser beam in a pulsed laser deposition coating technique. The target material is vaporized in the plasma plume and get deposited as a coating on the substrate. This method is simple as well as has the benefit of forming uniform coating thickness. The deposition parameters can also be controlled to develop a high crystalline coating [5]. The schematic diagram of the pulsed laser deposition coating technique is shown in Fig. 8. Dinda et al. [45] developed HA coatings on Ti6Al4V substrates by laser ablation of HA targets with a KrF excimer laser and achieved pure, adherent, and crystalline HA coating using combined pulsed laser deposition and post-annealing at 300 ºC.

The coating HA coatings exhibited more resistance to dissolution by SBF. Carbonated HA films prepared by Rau et al. [46] exhibited a hardness value of 5 GPa at 30 °C and 28 GPa at 700 °C. Ca/P atomic ratio of 2.0 - 2.2 was observed and the processing temperature greatly influences the coating

thickness. Gomes et al. [47] used 532 nm laser, 30 J/cm^2 fluences, 10^{-4} Pa vacuum environment, and room temperature for developing crystalline HA on any surfaces for dental application. Pulsed laser deposited fluor-carbonated hydroxyapatite coatings promote cell viability and antibacterial properties [48], [49].

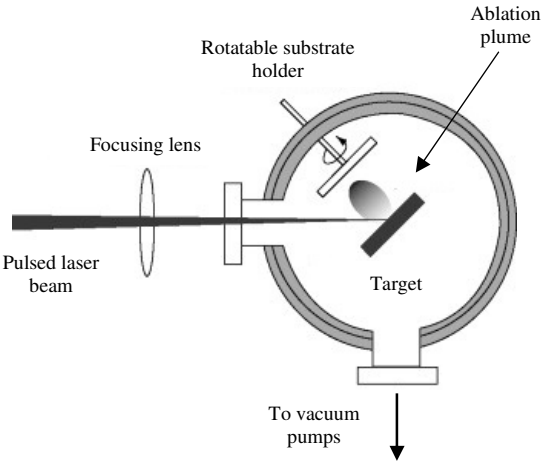

Fig. 8. Schematic diagram of the pulsed laser beam process [50].

2.4.Sol-gel technique

The technique of sol-gel is widely used in the synthesis of many inorganic materials as crystalline homogeneous films develop easily in comparatively low temperatures. Additionally, it is a simple and low-cost method as well as more convenient for making complex shape coatings. Kaygili et al. [51] used sol-gel technique to synthesize HA-based bioceramics with high Al contents and achieved an average crystallite size in the range of 10–50 nm and Ca/P ratio of 1.61. The properties of HA changed with the incorporation of Al^{3+} ions. Polycaprolactone/fluoride substituted-hydroxyapatite (PCL/FHA) nanocomposite coating developed on Ti6Al4V substrate using in-situ sol-gel process for dental implant applications [52].

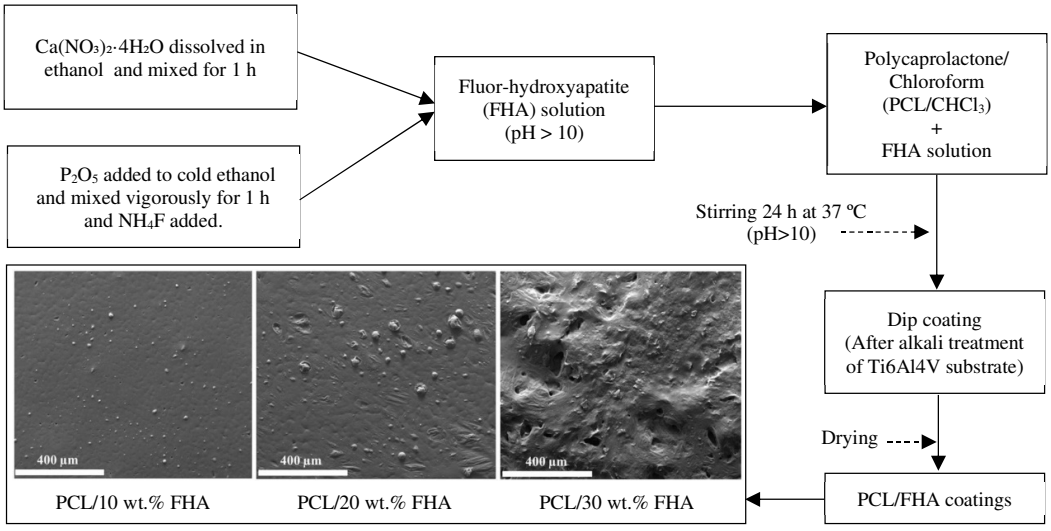

Fig. 9. Development of PCL/FHA coating using in-situ sol-gel process [52].

The methodology adopted for developing the coating is depicted in Fig. 9. With an increase in FHA content, the hydrophilicity, adhesion strength, and surface roughness of the coating can be increased. Reis et al. [53] investigated the microstructure and mechanical properties of mono and bilayer zirconia specimens infiltrated with silica by the sol-gel method for dental restorations and reported that Infiltration increases the structural homogeneity and hardness of the monolithic zirconia and reduces the fracture toughness. Combined sol-gel and dip coating methods were used to make HA coatings on titanium substrates [54]. The superior coating was obtained with the addition of a calcium titanate ($CaTiO_3$) sublayer on the titanium substrate as well as through additional preheating at 650°C.

2.5. Sputter coating technique

The sputter coating method is a vapour deposition method and is the release of a substance through energetic particle bombardment from the target into a substrate. The process begins with a sputtering cathode electrically charging, which turns into a plasma which causes the material to be ejected from the target surface. RF magnetron sputtering was used to develop Mn-coatings on the micro-pore Ti-29Nb-Hf alloys for dental applications [55]. DC magnetron sputtering was utilized for depositing TiAlN coatings with different propositions of Ag and Cu nanoparticles on 420 steel [56]. TiAlN(Ag,Cu) at 20 at.% exhibited a better bactericidal effect due to the presence of Ag-Cu particles (high quantity and large size). It was suggested that these kinds of coatings are most suitable for applications in surgical and dental instrumentation. The schematic representation of the magnetron sputtering process used for developing TiAlN(Ag, Cu) coating is as shown in Fig. 10.

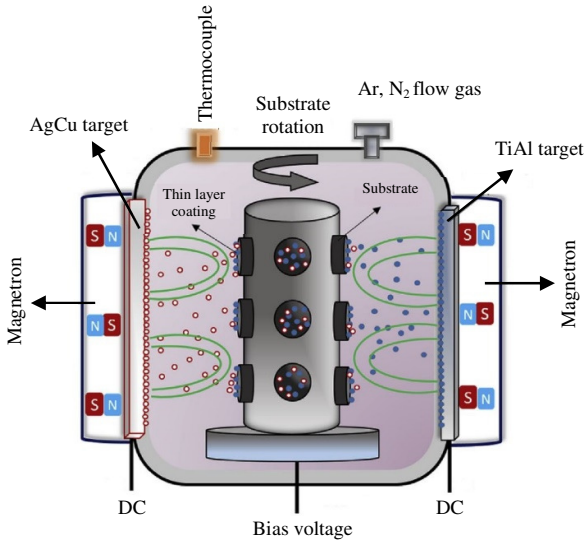

Fig. 10. Configuration of magnetron sputtering chamber [56].

3. Emerging functional coatings

3.1.Graded composition

These types of graded coatings feature varying chemical composition and microstructure along with the thickness of the substrate surface. This allows controlling the phase and microstructure leading to desirable properties. Often these coatings are further modified by carrying out heat treatment after primary deposition. The coating technique that is selected also affects the resulting properties of such graded architecture despite a similar chemical gradient [57]. For a coating to be durable, adhesion to the implant surface in addition to possessing the necessary mechanical properties such as hardness and

wear resistance is critical. While research on chemically graded coating is ongoing, the application of such coatings for dental implants was studied as earlier as 1997 [58]. The study used gradient titanium and hydroxyapatite and showed improved osseointegration with reduced inflammation. This was later confirmed by other studies which also showed excellent adhesion strength [59], elastic modulus, yield strength, and fracture toughness [60].

3.2.Graded porosity

Ti-based dental implants are widely used due to their mechanical performance, biocompatibility, and corrosion resistance. However, stress shielding [61], stiffness mismatch [62], and lack of functional porosity can negatively affect the implant-tissue interface. According to Miao and Sun [63], functionally graded coatings as shown in Fig. 11 offer a potential solution as they can be customised for pore density and size. The overall porosity and the associated gradation can be achieved by carefully modifying the characteristics of the feedstock material along with the processing parameters of the coating technique being employed.

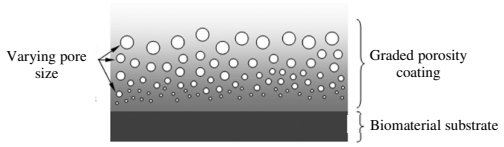

Fig. 11. Functional coating with graded porosity, adapted from [57].

The direction of porosity grading is dependent on the requirement of the dental implant. A variation in the porosity of the coating from top to bottom is suitable when there is a requirement for high mechanical performance and tissue integration. An inverse gradient in porosity is suitable for drug-loaded implants to improve bioactivity or infection resistance [64], [65]. Lastly, functional gradients can be suitable for implants at hard-soft tissue interfaces. Overall, the area of functional graded coating is growing and allows to improve the overall performance of dental implants in the years to come [66].

4. Limitations and future challenges

Despite biomaterial coating being an active field of research, very few materials, drugs or techniques are currently clinically available when it comes to using in dental implants. To translate research in the coating to the application requires extensive clinical studies regarding their long-term performance. The peri-implant infections and malfunction of the bioactive surface coating are also another area that requires thorough investigation. Insufficient interface performance of coatings leading to failure under mechanical stress also results in further complications and infections in dental implants [67]. It could also be argued that there is a higher chance of weak surface as elastic modulus, tensile strength, and fatigue behaviour of bioactive coatings are poor compared to substrates that lead to microcracks and fracture [68]. Another area is the emergence of metamaterials enabled by additive manufacturing that involve complex submicron porosity [69]–[72] that calls for innovation in coating technology and nanostructured coatings.

5. Summary

Different types of materials and coating techniques are being developed around the world for coating biomaterials suitable for dental applications as discussed thus far. Overall, Significant efforts are being directed to the development of coatings with superior biocompatibility and osteointegration as well as

having antibacterial properties. A substantial consideration is the surface characteristics of dental implants such as topography and surface chemistry. Several coatings have demonstrated that the surface characteristics of the implant can be altered or modified for better integration with the host tissue structure through encouraging growth and adherence of cells at the coated surface. Hydroxyapatite-based coatings seem to exhibit an increased differentiation of osteoblast-like mesenchymal stem cells and enhanced cellular adhesion, proliferation, and integration at bone titanium interface. More research in this field is needed to develop the ideal composite coating to achieve better mechanical and osteogenic properties with the resistive properties of infection. The development of optimum dental coatings can accelerate healing and restore normal function reducing the biological and financial burden associated with dental implants.

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