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Review

Surface modification of Ti6Al4V alloy via advanced coatings: Mechanical, tribological, corrosion, wetting, and biocompatibility studies

Ankit Kumar, Gurminder Singh *

Department of Mechanical Engineering, Indian Institute of Technology Bombay, Powai, Mumbai 400076, India

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ABSTRACT

Titanium alloys play a prominent role as metallic biomaterials in the biomedical sector, particularly for implant applications. Various types of Ti alloys are suitable for medical treatment, including Ti6Al4V (Ti64) alloys, which are extensively utilized in biomedical implant materials. This preference was attributed to their commendable strength, excellent corrosion and wear resistance, and satisfactory biocompatibility. Nonetheless, implants produced through diverse additive manufacturing (AM) methods or commercially available methods face performance-related challenges, including mechanical, wear resistance, corrosion resistance, wettability, and biocompatibility. To address these limitations, researchers have actively sought ways to enhance the implant performance. An effective approach to overcoming these challenges involves surface modification using advanced coatings. Therefore, this work provides a comprehensive review of various surface coating materials and techniques employed to enhance the mechanical properties, wear resistance, corrosion resistance, wettability, and biocompatibility of titanium alloys for biomedical applications. This review encompasses an array of coating materials, including metal nitrides (MNs), diamond-like carbon (DLC), high-entropy alloys (HEA), metal oxides (MO), and polymer–metal oxide (P-MO) composites. It offers detailed insights into the operational biomechanisms of various coatings, thoroughly discusses how and which type of coatings enhance biocompatibility, and provides valuable insights for advancing the field.

1. Introduction

In the constantly advancing realm of medical science and technology, a steadfast dedication to seeking inventive approaches to meet the intricate requirements of patients persists. The primary difficulties that arise with the regular use of metal implants in the human body include their high wear resistance, sensitivity to corrosion, and ability to blend with surrounding tissues. Stainless steel, titanium, magnesium, and cobalt-chromium are notable materials, and their alloys are widely used in biomedicine [1,2]. This endeavor also includes the development of bio-implants and improved prostheses, where notable advancements have been made owing to the combination of biomedical knowledge and engineering inventiveness [3]. Notably, the advent of Additive Manufacturing (AM) and rapid prototyping technologies has triggered a transformative shift in the production of customized biomedical implants, particularly those constructed from titanium alloys, including Ti6Al4V [4,5]. The evolution of titanium (Ti) and its alloys, with Ti6Al4V alloy at the forefront, has been nothing short of remarkable, catapulting these materials to prominence in a wide range of high-end industrial applications. Industries in the aerospace, biomedical, and power/energy sectors benefit from the exceptional properties of these materials [5]. Ti and its alloys exhibit a unique combination of attributes, including remarkable corrosion resistance and specific strength, which are the highest among all metallic elements, coupled with a relatively low density [6]. Furthermore, their specific strength remains impressive even at elevated temperatures [7]. The challenges of Ti6Al4V alloys, like many exceptional materials, stem from their inherent machining difficulties. In particular, they exhibit thermal softening at high temperatures, which sets them apart from more traditional metals, such as steel or aluminum and alloys [1,8]. Titanium and its alloys also exhibit intricate deformation mechanisms [9]. This unique property, along with the low thermal conductivity and volume-specific heat in Ti-alloys, leads to high cutting temperatures during machining [10]. High temperatures lead to tool wear, prompting extensive research and development in AM processes as a promising alternative for producing titanium alloys [11].

The allure of AM extends from its ability to create intricate geometries with precision, rendering it a compelling choice for fabricating

* Corresponding author.
E-mail addresses: Gurmindersingh2012@gmail.com, Gurminder.singh@iitb.ac.in (G. Singh).

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customized prostheses and bio-implants tailored to individual patient needs [12]. This is further accentuated by its rapid journey from design to manufacturing, streamlining modifications, and implantation, which significantly reduces the manufacturing time compared to conventional methods. Many steps in conventional methods, such as molding, forming, machining, melting, and shaping, can be circumvented using AM. AM's ability of AM to manufacture near-net shapes [13] minimizes the need for extensive machining to achieve excellent surface finishes and shapes, particularly in biomedical applications [14,15]. This not only makes the process cost-effective but also marks a substantial leap in the realm of biomedical implant manufacturing [6,16].

As the medical community embraces the potential of titanium alloys, more specifically Ti64, in the realm of biomedical applications, the focus has shifted toward optimizing their performance and biocompatibility [16,17]. Despite the vast potential of these materials, implants produced using various AM methods present unique challenges. Wear resistance, corrosion resistance, wettability, and cytotoxicity are primary concerns [18,19]. Furthermore, the disparity in mechanical properties, specifically the hardness and elastic modulus, between the Ti64 alloy and human bone can give rise to a phenomenon known as stress shielding [20]. This phenomenon has the potential to disrupt the natural growth and healing of bone tissue, thereby diminishing the biocompatibility of the implants. Moreover, the absence of inherent antibacterial properties in the Ti64 alloy often results in post-implantation bacterial infections, which are common and lead to a host of clinical complications, ultimately jeopardizing the success of implantation and the well-being of patients [10,21]. It is worth noting that addressing these issues often necessitates antibacterial treatments, secondary surgeries, and reimplantation, all of which significantly increase the financial burden on both patients and the healthcare system. Consequently, these shortcomings compel researchers to explore avenues for improvement and innovation.

Surface modification with bioactive coatings is a viable solution for biocompatibility-related issues [22]. These coatings are designed to enhance biocompatibility by promoting cell growth and optimizing the functionality of Ti64 implants, making them a focal point of current research [23]. The surface properties of implants are crucial in determining their biological responses within the body. For instance, bone implants must exhibit superior bone formability for successful biological integration, whereas blood-contacting devices such as heart valves require exceptional blood compatibility [24,25]. Other prosthetic and orthopedic implants require enhanced resistance to corrosion, wear, and superior osseointegration [26]. The tailored surface properties of biomaterials improve tissue-material integration while minimizing adverse reactions [23,27]. Effective surface modification techniques maintain the implants' excellent bulk properties, including modulus and strength, while enhancing their essential surface properties [23,25,28]. The prudent selection of coating techniques, materials, morphology, and structural composition of these coatings can effectively confer the specific surface properties required to meet the targeted requirements of the intended application. Overall, by resolving a number of issues related to bio-implant interactions with the biological environment, coatings can significantly improve the biocompatibility and performance of these materials. [20,29].

This comprehensive review provides an in-depth exploration of various advanced coating techniques and materials utilized for surface modification in biomedical applications [30,31]. It places specific emphasis on the commercially available and additive manufactured (AM) Ti64 implants, encompassing various AM methods such as PBF-LB/M, PBF-EB/M, BJ, and DED [10,32]. The coating materials discussed include transition metal nitrides [33,34], diamond-like carbon (DLC) [35,36], medium/high-entropy alloys (HEA) [37,38], inorganic-polymer composites [39,40], and metal oxide-based biocompatible coatings [33,41,42]. This review places a central focus on biocompatible coatings and their properties, including their mechanical, tribological, corrosion, wettability, and biological characteristics, which are essential for biomedical applications. This review serves as a comprehensive resource, encapsulating the entire journey from the manufacturing of titanium alloys to the coating properties and their application in the biomedical field. The graphical abstract and organizational flow of this review are illustrated in Fig. 1.

2. Biocompatibility of titanium alloys (Ti6Al4V)

Biocompatibility refers to the capacity of a material to interact with biological systems without inducing harm or undesirable reactions. Biocompatibility is of paramount importance in the context of medical devices, implants, or materials that come into contact with the human body [43]. Biocompatible materials are designed and tested to ensure that they do not induce toxic, allergic, or immunological reactions when in contact with bodily tissues or fluids [44]. These materials should be compatible with the human body, allowing for proper integration, minimal inflammation, and appropriate biological responses [45]. Ensuring biocompatibility is essential for the safety and effectiveness of medical implants, devices, and materials used in healthcare and biomedical applications [46,47]. Ti64 alloy is extensively used in the medical field owing to its distinct mechanical characteristics and compatibility with biological systems.

Ti6Al4V, alternatively known as TC4, Ti64, or ASTM Grade 5, is an alpha-beta titanium alloy, which is celebrated for its exceptional specific strength and corrosion resistance [48]. It comprises approximately 90% Ti, 6% Al, 4% vanadium, and trace elements. The key trace elements that play a vital role in enhancing titanium's properties include niobium (Nb), molybdenum (Mo), zirconium (Zr), and tantalum (Ta) [49,50]. The notable features of this alloy include its significant strength, low density, and outstanding corrosion resistance. In biomedical applications, Ti64 takes precedence in the creation of orthopedic implants, dental prosthetics, and various medical devices [21,51].

The bulk raw materials are forged, rolled, and cast in traditional Ti6Al4V product manufacturing processes, and the final forms and dimensions are achieved through additional machining [10]. Unfortunately, these conventional processes result in a significant amount of material waste, high manufacturing costs, and extended lead times [7]. Considering these challenges, AM is an advanced manufacturing process that creates near-net shape structures directly from computer-aided design (CAD) models by incrementally adding materials layer by layer. This method is highly advantageous for producing intricate biomedical implants made of Ti64 [52]. Powder-based processes in the field of metal AM technologies are increasingly gaining significant attention, particularly in biomedical applications. These technologies include powder bed fusion (PBF) and direct energy deposition (DED). The energy source could be laser and electron beam. The popular laser based process is selective laser melting (SLM) and electron beam based process is electron beam melting (EBM). The SLM and EBM powder bed fusion based processes are being increasingly used in the biomedical sector due to their capacity to fabricate intricate shapes with micro and macro features [53]. DED process is not commonly used for fabricating medical implants due to their higher layer thickness. Post processing of machining is required to get accurate shape and features [54]. Additionally, binder jetting (BJ), extrusion based 3D printing (E3D) and rapid tooling (RT) in combination with sintering have been used to fabricate medical implants [2,55,56]. As to the ASTM F2792 - 12(2018) standard, "the powder bed fusion (PBF), which includes selective laser melting (SLM) and electron beam melting (EBM) methods [57]. These processes are cheaper as compared to laser and electron beam based processes. Furthermore, ongoing research has delved into post-processing techniques for additively manufactured components, aimed at enhancing their mechanical and biological properties to make them suitable as biomaterials. These post-processing methods include Hot Isostatic Pressing (HIP), machining, polishing, and various coating techniques [58]. For a comprehensive summary of additively manufactured biomedical products based on Ti6Al4V, one can reference

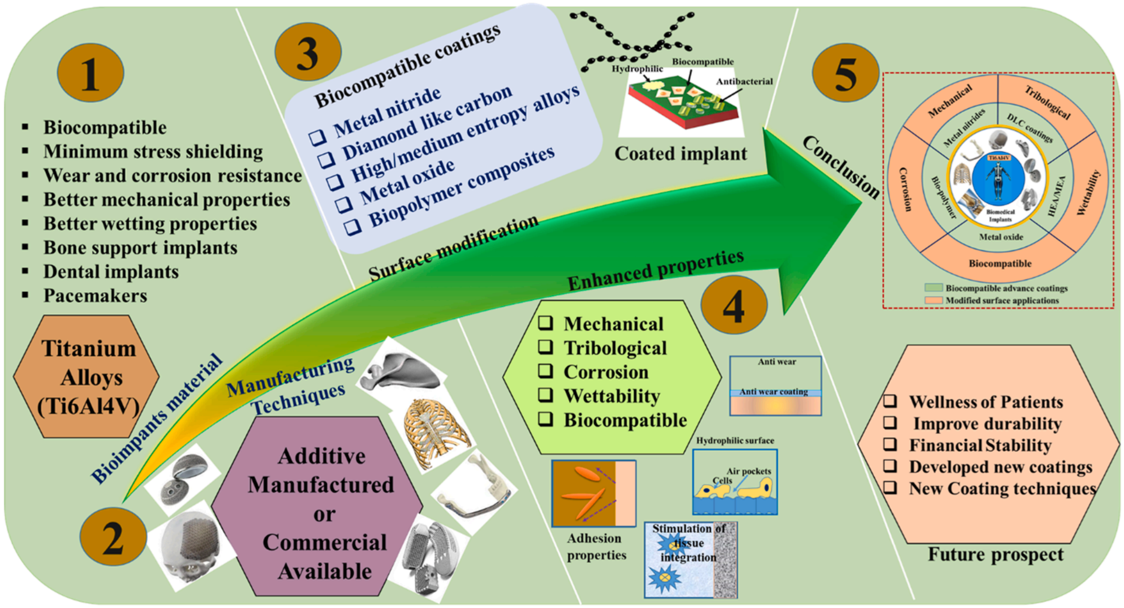

Fig. 1. A schematic representation illustrating the graphical abstract and workflow shows the improved properties of a coated Ti6Al4V implant in a systematic review.

Table 1
Some applications of various additive manufacturing techniques-based titanium biomedical products, as Mechanical, wetting, tribological and biocompatible applications.

Titanium Alloys	Manufacturing techniques	Mechanical Properties, Contact angle	Wear and Corrosion Properties	Biomedical properties	Ref.
Ti6Al4V	StandardSLM	(110 GPa, 930 MPa & 860 MPa)	-	Better biocompatibility	[60]
Ti6Al4V	Selective electron beam melting (SEBM)	15 GPa & 129 MPa	-	Replacement for human cortical and cancellous bone	[61]
Ti6Al4V	Electron beam melting (EBM)	30 MPa, 200 MPa	-	-	[62]
Ti6Al4V	Laser and Electron Beam	1246 MPa & 972 MPa	-	Knee and hip stronger	[63]
Ti6Al4V-xCu	Selective laser melting (SLM)	-	CR (0.669–0.119)	Antibacterial, cytocompatibility replacements	[64]
Ti6Al4V	Selective laser melted	-	E_{corr} (-467−101) mV I_{corr} (45.03–249.66) nA/cm^2	Dental applications	[65]
Ti6Al4V	SLM	0.58–2.61 GPa, 8.6–36.5 MPa	-	Orthopedic or porous implants	[66]
Ti6Al4V	Powder bed fusion	428 HV, 1310 MPa, 1193 MPa	-	Biocompatible applications	[67]
Ti6Al4V	SLM	-	-	Bone tissue repair	[68]
Ti6Al4V	SLM	-	-	Good osseointegration	[69]
Ti6Al4V, Ti6Al4V-TiC composite	EBM	-	E_{corr} (-225.60–331.43) mV I_{corr} (25.57–5.674) nA/cm^2	-	[70]
Porous Ti6Al4V	EBM	10.37–43.33 GPa	-	Bone regeneration and Neovascularization	[71, 72]
Ti6Al4V and Laser treated	Commercial	599 HV, Decreasing wear rates of 89.79 and 85.43%, CA=78°-20°	COF=0.435–0.215	Vitro bioactivity	[73]

Table 1 lists their mechanical, wetting, tribological, and biocompatible applications. Fig. 2 depicts illustrations of Ti64 alloy implants utilized in diverse regions of the human body, showcasing better biocompatibility.

3. Advance surface modification and biocompatible coatings for Titanium alloys bio-implants

Fig. 3 provides a comprehensive representation of the enhanced biocompatibility of bioimplants, specifically focusing on various key properties, including mechanical strength, tribological characteristics, wetting behavior, corrosion resistance, and overall biocompatibility. The improvements observed are attributed to the utilization of advanced biocompatible coatings, such as metal nitrides, DLC (diamond-like carbon), high entropy alloys, metal oxides, and bio-polymer composite coatings, among others. These coatings are crucial for enhancing the performance and functionality of bioimplants, providing superior mechanical and tribological properties as well as improved wetting behaviour and corrosion resistance. The synergistic effect of these coatings results in bioimplants that exhibit enhanced biocompatibility, making them more compatible and responsive within the biological environment. This figure serves as a visual testament to the positive impact of advanced biocompatible coatings on the multifaceted properties of bioimplants, further emphasizing their potential for advancing biomedical applications.

A schematic image showing the arrangement and makeup of the hard tissues in the human body is shown in Fig. 4. This detailed depiction

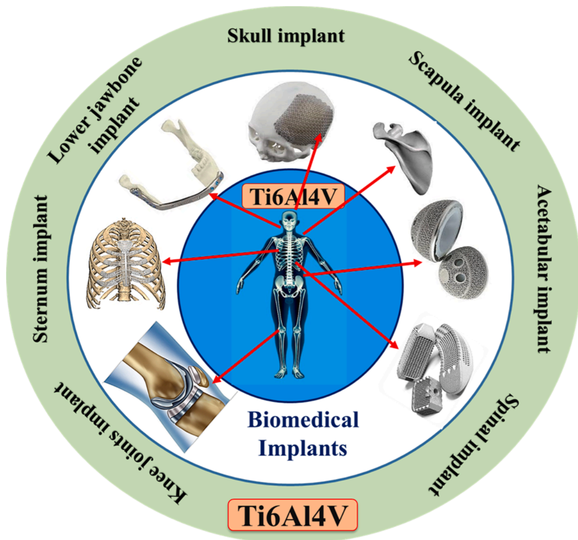

Fig. 2. Functionalizing the interface of 3D-printed and commercially available titanium alloy implants for enhanced biomedical field applications [59].

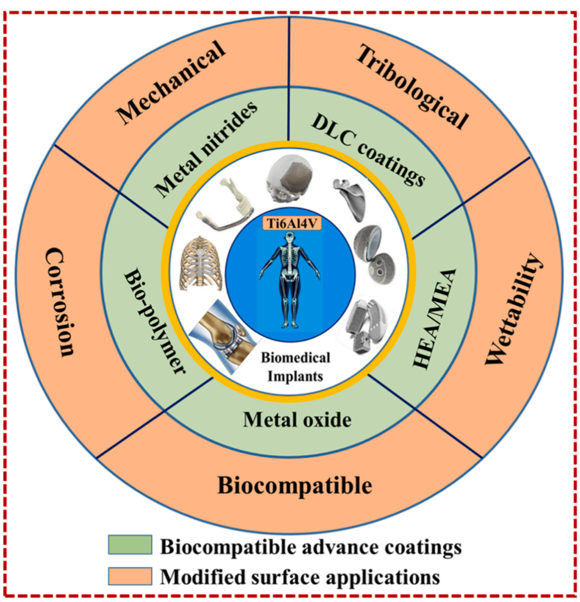

Fig. 3. A schematic representation illustrating the enhanced properties of a coated Ti6Al4V implant.

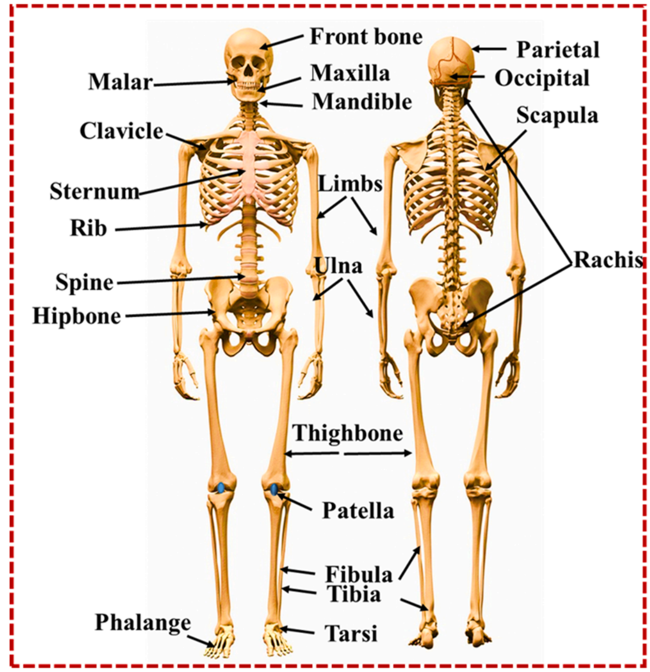

Fig. 4. Schematic representation depicting hard tissues within the human body that can be replaced in the event of accidental damage.

provides a visual overview of the spatial relationships and configurations of various hard tissues, offering valuable insights into the intricate framework that comprises the skeletal system. The schematic captures the complexity and interconnectedness of hard tissues, including bones and other anatomical structures, providing a comprehensive representation that aids in understanding the anatomical composition of the human body. This diagram serves as a valuable tool for researchers, healthcare professionals, and students, facilitating a clearer comprehension of the spatial organization of hard tissues and their role in supporting and shaping the human body.

Hard tissues often incur damage due to accidents, aging, and other factors, necessitating surgical interventions to replace them with artificial substitutes. The choice of endoprosthetic materials varies depending on the implantation regions and required functions. Titanium and its alloys stand out as extensively utilized materials in biomedical applications, serving as effective replacements for hard tissues, particularly in cardiac and cardiovascular contexts. This preference is attributed to their desirable properties, including a relatively low modulus, machinability, excellent fatigue strength, corrosion resistance, formability and biocompatibility. Consequently, titanium and its alloys find widespread use in the fabrication of dental implants, artificial bones and joints, addressing the diverse needs for hard tissue replacements.

For each replaceable hard tissue represented in Fig. 4, we have provided Table 2 with an explanation explaining the appropriate coatings for the different replaceable hard tissues shown in Fig. 4 that are made using additively manufactured Ti6Al4V implants. The discussion takes into account factors like wear, corrosion, dynamic and static loading, and so on. Additionally, scientific considerations are taken into account when selecting appropriate surface modification through various coatings. Biomedical engineering perspectives on surface modification technologies for titanium and its alloys encompass a range of methods, including thermal spraying, mechanical treatment, sol-gel processes, electrochemical as well as chemical treatment, along with ion implantation. Examining these approaches reveals their potential to selectively improve wear resistance, corrosion resistance, and biological properties of titanium and its alloys. This recent research underscores that by employing appropriate surface treatment techniques, these improvements can be made without sacrificing the materials desired bulk properties [26,27].

The selection of coatings for Ti6Al4V implants made by additive manufacturing that are intended to accommodate different replaceable hard tissues is contingent upon multiple parameters, such as wear resistance, corrosion resistance, dynamic/static stress, and biocompatibility [59]. Diamond-like Carbon (DLC) coatings are appropriate for load-bearing applications on bone implants because of their superior wear resistance and biocompatibility [76]. Inorganic-Polymer Composites, on the other hand, provide cartilage with the cushioning and flexibility needed to preserve joint function. Because of their exceptional hardness and resistance to corrosion, transition metal nitride is the preferred material for dental implants [79,86]. Because they combine strength and flexibility in just the right amounts, High-Entropy Alloys (HEA) are a good choice for ligament replacements. Because they are corrosion-resistant and have good biocompatibility, metal oxides are appropriate for joint applications [37].

Scientific considerations for choosing coatings include

Table 2
Suitable coatings for additively manufactured Ti6Al4V implants for different replaceable hard tissues.

S. No	Replaceable Hard Tissue	Suitable Coating	Dynamic/ Static Loading	Corrosion Resistance	Wear Resistance	Scientific Considerations	Ref.
1.	Hip replacement	Diamond-like Carbon (DLC)	⁎	††	††	DLC offers excellent biocompatibility and wear resistance, making it suitable for load-bearing bone implants.	[74–76]
2.	Cartilage	Inorganic-Polymer Composites	⁎⁎	†	†	Composite coatings provide cushioning and flexibility, beneficial for cartilage applications	[77,78]
3.	Teeth, Orthopaedic implants	Transition Metal Nitrides	⁎	††	††	Nitride coatings offer excellent hardness and corrosion resistance, ideal for dental implants and orthopaedic implants	[79–81]
4.	Ligaments, hip, knee replacement and cardiovascular	High-Entropy Alloys (HEA)	⁎⁎	†	††	HEA coatings provide a balance of strength and flexibility, suitable for ligament, hip and knee replacements.	[37,82,83]
5.	Cervical disc and Joints	Metal Oxides	⁎	††	††	Metal oxide coatings offer good biocompatibility and corrosion resistance, suitable for Cervical disc and joint applications.	[84,85]

High- ††, Dynamic- ⁎⁎, Moderate- †, Static- ⁎

understanding the mechanical properties of the tissue, the nature of the surrounding environment (e.g., exposure to bodily fluids), and the desired lifespan of the implant. The selection of coatings has to be predicated on their capacity to endure the distinct biomechanical strains and corrosive conditions linked to every replaceable hard tissue. For ideal tissue integration and long-term implant success, factors like surface roughness, porosity, and cellular responsiveness should also be assessed [87].

Therefore, surface modification of implanted coated biomaterials offers a feasible approach to improve biocompatibility and reduce related infection rates. Biomaterials are often modified on their surface without affecting the micro/nano-scale characteristics of the substrate. Surface coating allows surface features of biomaterials to be simultaneously controlled and regulated, while also providing beneficial chemical or physical properties that make implanted biomaterials "more compatible" with the human body. These methods can be used separately or in combination, each with its own advantages and disadvantages. The surface characteristics of modern materials are usually not sufficient to cope with wettability, adhesion, and biocompatibility; therefore, they need to be modified before being applied or after any further processing, such as advanced coatings for functional materials [23,88]. Several surface modification coatings have been developed, as illustrated in Fig. 5, with the goal of improving the wear resistance, antibacterial properties, biocompatibility, corrosion resistance, and other features of Ti6Al4V to fulfil the demands of clinical diagnosis and treatment [23]. It is clear that the five main categories of metal nitrides, DLC coatings, high/medium entropy alloys, metal oxides, and biopolymer coatings are further broken down into a number of smaller groups for additional categorization.

Fig. 6 shows how different surface treatments applied to metallic implants made through additive manufacturing affect interactions through coatings after insertion. Several biocompatible coatings have been proposed to prevent bacterial colonization of implanted biomaterials, particularly in orthopedic applications. However, their widespread adoption faces challenges, such as bacterial resistance, bone integration issues, regulations, and costs. A promising solution is a rapidly resorbable hydrogel coating loaded with antibacterial agents. This coating offers several advantages: it effectively prevents early bacterial colonization post-surgery, ensuring crucial protection during vulnerability; it is safe, with high local antibacterial concentrations, minimizing resistance risks and adverse effects on bone healing; it is adaptable for mixing with various antibacterial agents intraoperatively, easy to handle, and potentially cost-effective for large-scale use. Coatings also play a significant role in influencing the interactions with proteins, cells, and pathogens on biocompatible surfaces. They can modulate protein adsorption, reduce inflammation, and improve overall biocompatibility. Additionally, they may deter cell attachment to prevent issues such as fibrous encapsulation and act as barriers to pathogen colonization, releasing antimicrobial agents to inhibit growth and prevent biofilm formation, ultimately enhancing long-term performance [89].

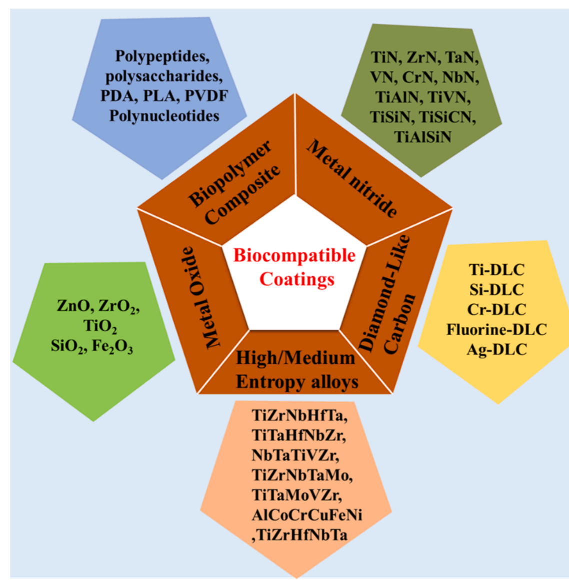

Fig. 5. Various advanced surface-modification coatings and their classification to improve Ti6Al4V alloy implants.

3.1. Metal nitrides (MNs) biocompatible coatings

Metal nitrides (MNs) are interstitial metallic compounds in which the nitrogen atom is integrated into the interstitial sites of the parent metal, conferring covalent and ionic properties. These materials exhibit distinctive electronic structures, exceptional mechanical robustness, enhanced chemical stability, and high electrocatalytic activity. MNs stand out for their ability to combine metallic and nonmetallic characteristics, resulting in unique properties that make them valuable in various applications. This integration of nitrogen into the metal lattice not only imparts specific functional attributes, but also contributes to the overall versatility and performance of metal nitrides, making them a subject of significant interest and exploration in materials science and

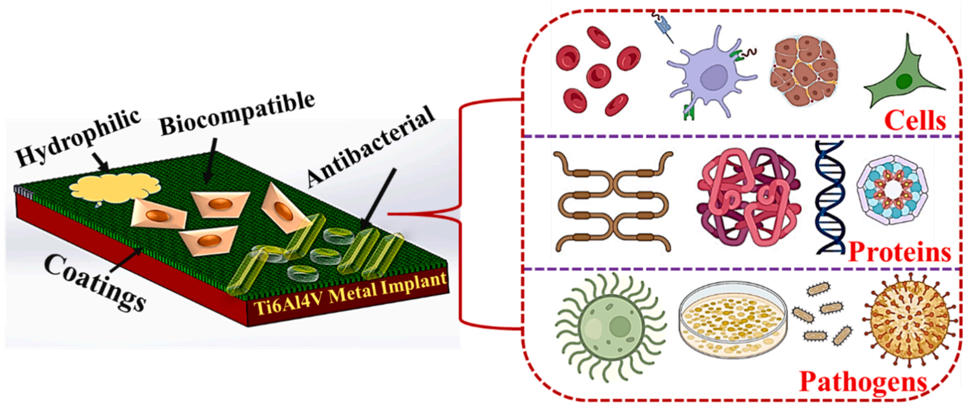

Fig. 6. Diagram illustrating the controllability of the interactions between Ti6Al4V implants after implantation using different surface modifications (BioRender.com).

engineering. MNs coatings have attracted the interest of researchers owing to their advantageous characteristics, including superior resistance to corrosion, hardness, biocompatibility, and wear resistance. Binary or ternary nitrides of transition metals have excellent mechanical, tribological, corrosion-resistant, and biocompatible characteristics [90]. Nitride coatings such as titanium nitride (TiN) [33,91–93], titanium aluminum nitride (TiAlN) [34], titanium silicon nitride (TiSiN) [94], TiSiCN [95], titanium carbon nitride (TiCN) [96], niobium nitride (NbN) [97], chromium nitride (CrN) [97,98], zirconium nitride (ZrN) [99,100], gallium nitride (GaN), tantalum nitride (TaN) [101], vanadium nitride (VN), hexagonal boron nitride (h-BN)[102] and titanium vanadium nitride (TiVN) [103] [104] are considered appropriate for use as protective coatings on implants, either as single or multilayer systems, with the goal of extending their longevity by reducing corrosion and wear. In Fig. 7, various advanced nitride coatings are prominently featured, illustrating their application in the surface modification of Ti6Al4V orthopedic bio-implants. Visual representation provides insights into the diverse biomedical settings in which these coatings are utilized to enhance the properties of orthopedic implants. This figure serves as a valuable resource, showing the versatility and practical applications of advanced nitride coatings in biomedical engineering. The coatings displayed are strategically employed to modify the surface characteristics of Ti6Al4V implants, indicating their potential impact on improving the performance, biocompatibility, and overall functionality in orthopedic applications.

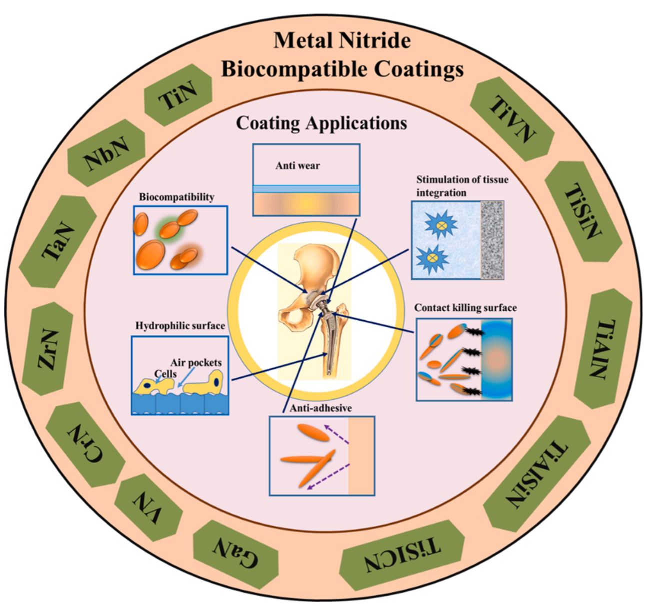

Fig. 7. Different advanced nitride coatings have been employed to modify the surface of Ti6Al4V orthopedic bio-implants and their applications in various biomedical settings.

3.1.1. Mechanical properties of Metal nitrides (MNs) coated Ti6Al4V alloy

To achieve this, it is necessary to examine the impact of the metal nitride layer on the mechanical properties of the alloy, such as its elasticity, hardness, and strength. Determining whether the coating improves Ti6Al4V overall mechanical performance is the goal because implants used in biomedical applications must be able to endure mechanical forces inside the body. Through assessment of the Ti6Al4V mechanical characteristics, scientists hope to create stronger, more dependable, and long-lasting medical implants that can better endure daily use and enhance patient outcomes [24] [105]. Coatings with many elements and layers are used to increase the film thickness and hardness without sacrificing brittleness or lowering the yield strength [24]. Achieving ideal mechanical and tribological qualities requires careful consideration of the element composition, layer materials, and coating design, including the shape, size, and layer thickness [24]. Table 3 presents the mechanical characteristics of the diverse nitride coatings, offering a comprehensive overview of their properties.

Fig. 8 shows that the highest penetration depth for bare stainless steel was 55 nm at a load of 0.8 mN. The anticipated contact area A was used to calculate the material hardness to reduce issues with tiny, permanent indentations in nanoindentation experiments. The samples with uncoated steel, Ti6Al4V, and TiN coating (both steel and Ti6Al4V) had hardness values of 7.5 ± 0.7 GPa, 9.6 ± 1.1 GPa, and 27.4 ± 4.0 GPa, respectively, while TiZrN had a hardness value of 27.0 ± 3.7 GPa. The thickness of the TiN coating deposited on 316LVM stainless steel measures 1.48 ± 0.03 μm, while on Ti6Al4V ELI titanium alloy, it measures 1.46 ± 0.03 μm. Although thicker coatings often correlate with greater hardness, the relationship between coating thickness and hardness is intricate, influenced by diverse factors such as material properties, deposition method, and intended application [106]. Moreover, the increased hardness resulting from the TiN coating can be explained by the following: decreased crystallite size, improved energy absorption during loading, and valence charge transfer. Additionally, no creep was observed in the TiN coating, which is important for self-locking screw joint designers because creep in mating materials can lead to the rotational loosening of screws [106].

The good mechanical properties of coatings are defined by high hardness, toughness, adherence to the substrate, minimal friction, thermal and chemical stability, and load-bearing capabilities in biomedical and tribological applications. Hardness is considered to be the most important characteristic. The recommended technique for assessing the nanohardness and investigating the Young's modulus of

Table 3
The properties of nanostructured nitride coatings on commercially available Ti6Al4V substrates and additively produced (AM) products have been studied in previous studies.

Nitride Coatings	Coating Techniques	Mechanical and Wetting Properties	Wear and Corrosion Properties	Biocompatible coatings	Ref.
HA/TiN	Chemical Vapor Deposition (PACVD)	-	E_{corr}-(-469–149) mV I_{corr}-(0.27–0.6) nA/cm^2	Cell viability and proliferation	[134]
TiN, TiN-O_2, TiN-g, TiN-g-BMP2	Impulse magnetron sputtering technique	TiN (73.2°) Ti6Al4V (68.7°), TiN-g (36.4°), TiN-O_2(<10°) TiN-g-BMP2 (51.5°)	E_{corr}-(-454.30–336.99) mV I_{corr}-(0.45–11.82) μA/cm^2	vivo biocompatibility	[123]
TiN, ZrN CrN/TiN and CrN/ZrN	CAE-PVD coatings	75, 66, 80 and 63°	E_{corr} (-0.17–0.03) V I_{corr} (1.73–1.21)×10^{-3}A/cm^2	Bone-like apatite formation	[121]
TiAlN	Magnetron sputter ion plating process	Ti6Al4V-4.8 GPa, TiAlN-18.8–44.1 GPa	COF-0.45, Wear rate-49.5×10^{-14} m^3/N.m CoF-0.23, 1.37×10^{-14} m^3/N.m I_{corr}-1.74×10^{-9}A/cm^{-2}	Surgical implants	[34]
TiN	Cathodic arc-PVD	Ti6Al4V-5.27 GPa, TiAlN-38.63 GPa	COF=0.448 E_{corr} (-0.256) V I_{corr} (3.21–1.21) ×10^{-8}A/cm^2	Orthopedic implants	[137]
ZrCN and ZrCHfN	Magnetron sputtering	22.8–24.3 GPa	COF=(0.19–0.29) E_{corr} (-376–240) mV I_{corr} (0.67–0.04) ×10^{-8} μA /cm^2	Orthopedic systems	[138]
ZrN	Ion-plasma vacuum-arc deposition	-	-	Improved surgical outcomes and implant	[139]
HA/CTS/COL/h-BN	Electrophoretically deposited	1.185 GPA	COF=0.366, E_{corr}= (-0.174) V I_{corr} =7.75×10^{-9}A	Biomedical implants.	[140]
c-NbN	Magnetron sputtering	78.7°	-	Dental implants	[141]
TiN, TiON, and TiAlN	Magnetron sputtering	-	E_{corr} (-0.198—0.128) V I_{corr} (1.34–0.28) A/cm^2	Cytocompatbility with cell	[90]
TiVN	Magnetron sputtering	15.6 GPa	COF=0.35, I_{corr} (2.54) μA/cm^2	Good cell viability.	[104]
CrN and CrNiN	Magnetron sputtering	11.73–12.14 GPa	COF= 0.52 and 0.56 Wear volume= 1.47×10^{-3} –2.14×10^{-3} mm^3	-	[142]
TiAlN	Cathodic arc evaporation	44.4 GPa, 86.27°	150 mV	Biomedical applications	[119]
TiZrN	Magnetron sputtering	-	Wear rate= (10^{-8}–10^{-7}) mm^3/Nm E_{corr} (-332.9) V I_{corr} 84.5×10^{-9}A	Biomedical applications	[143]
TiN/TiO_2	Vacuum cathodic arc	9.02–13.05 GPa	COF-0.37–0.38, E_{corr}-(-74–68) mV I_{corr}-(68–54) nA/cm^2	Human osteoblast	[133]
TiN layer	Nitride treatments	~1.7 GPa to 8.6 GPa	COF-0.34–0.29, Wear rate = 18.27 × 10^{-6} mm3/N·m to 0.33 × 10^{-6} mm^3/N·m	In vitro bio-tribological	[122]
TiN	In situ selective laser gas nitriding	7.5 GPa–9.5 GPa	-	-	[144]
TiB–TiN	Laser deposition.	170 ± 5 GPa to 204 ± 14 GPa.	1.51×10^{-4} mm^3/Nm, 1.90×10^{-6} mm^3/Nm, and 1.90×10^{-6} mm^3/Nm	Orthopedic implants.	[145]

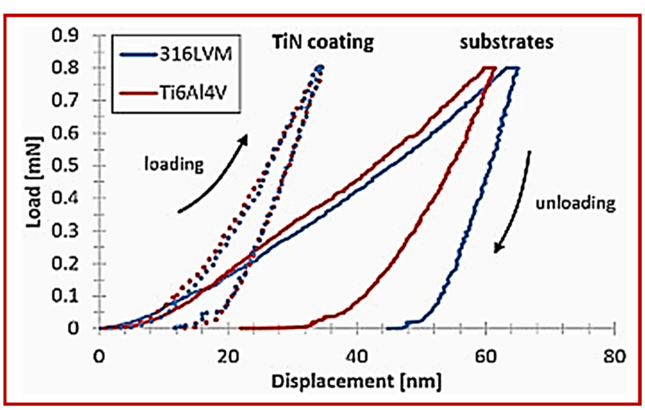

Fig. 8. shows the load-displacement curves obtained from nanoindentation measurements for both bare substrates and TiN-coated specimens [106].

coatings is nanoindentation, which uses a Berkovich diamond indenter tip. To create loading and unloading profiles, this method entails applying increasing loads to the tip, creating indentations on the thin-film surface, and measuring the related displacement [107]. The hardness and elastic modulus were determined using the load-displacement curve as a foundation. When TiN films were observed in a study by Babinova et al., the peak hardness was 30 GPa. Moreover, the high discharge current density and low nitrogen flow rate that led to the production of these TiN films resulted in a Young's modulus of 300 GPa [108].

The nanoindentation properties of TiAlSiN, TiAlN, TiN, and thin films were examined by Kong et al. The three materials were found to have different levels of hardness: 7.09 GPa for TiN, 15.6 GPa for TiAlN, and 21.7 GPa for TiAlSiN. Additionally, the sequence TiN > TiAlN > TiAlSiN was followed by the plastic deformation and elastic modulus energy. They also noticed that the hardness of the substrate affected the coating adhesion, with increased substrate hardness associated with better adhesion [109] [110]. To improve the scratch resistance of the Ar-ion-irradiated ion-implanted Ti6Al4V, multilayer TiN/Ti coatings were applied. A maximum adhesion strength of 72 N was observed for these coatings, which demonstrated remarkable performance. Additional experiments using nanoindentation have found that these coatings have a Young's modulus of 365 GPa and a hardness of 27.06 GPa [111]. Researcher Ni et al. [112] surface modified by TiN and TiCrN coatings on SLM fabricated Ti64 product had excellent hardness (TiN = 2100 HV, TiCrN = 2200 HV). The combination of B and Al results in both fine-grained strengthening and solution strengthening, which is why the AlCrBN coating has the maximum hardness of 37.2 GPa, exceeding the hardness of both CrBN (25.9 GPa) and AlCrN (30.6 GPa) coatings. However, in terms of adhesion strength, AlCrN performed better than CrBN (20 N) and AlCrBN (21 N) coatings, with a measurement of 45 N. The reason for the improved adhesive strength of AlCrN is its significantly higher hardness and thicker coating [113].

Multi-layer and composite coatings (due to grain refinement) exhibit superior resistance to fracture and wear, with a higher critical load compared to monolayer coatings, as indicated by previous research [114]. This has led to growing interest in advanced coatings. The properties of plasticity, hardness, and elastic modulus in multilayer coatings fall within the spectrum of relevant characteristics for each individual layer [113]. According to the literature, the mechanical characteristics of coated bioimplants are superior to those of bare surfaces. Consequently, the hardness of the binary-coated samples (TiN or ZrN) at 24.3 GPa is lower than that of the ternary-coated specimens (TiVN, TiAlN) [103] due to doping. Several factors explain the difference in hardness: a decrease in crystallite size, mixing entropy, valence charge transfer, and greater energy absorption during loading and release during unloading. Surfaces that exhibit dislocation and atom diffusion inhibition are characteristic of these coatings [115,116]. Finally, hard coatings can provide durability and resistance to surface damage. In applications such as orthopedic implants, where materials face constant friction and loading, a hard coating can prevent wear and improve the overall lifespan of the implant.

3.1.2. *Tribological properties of MNs coated Ti6Al4V alloy*

In the realm of biomedical engineering, biotribology has emerged as a crucial element in the design of diverse biomedical devices, ranging from artificial joints to implants and cardiovascular valves. The tribological properties of biocompatible metal nitride-coated Ti6Al4V fundamentally examine the material performance in terms of wear, lubrication, and friction, particularly in biomedical applications. This interdisciplinary field is dedicated to understanding the complex interactions between biological systems and tribological factors, and delving into the intricacies of friction, tension levels, and liquid cohesion within these devices. In particular, biomedical implants, such as joint replacements, endure repetitive mechanical stress. Coatings with elevated wear resistance play a pivotal role in minimizing material loss and mitigating the risk of debris generation. This is indispensable for ensuring prolonged and effective long-term performance of implants.

Alanagh et al. [67] applied hard ceramic coatings of titanium silicon nitride (TiSiN) to a Ti6Al4V bio-alloy using the pulsed-DC plasma-assisted chemical vapor deposition (PACVD) process. The purpose of this action is to increase the resistance of the alloy to corrosion and wear

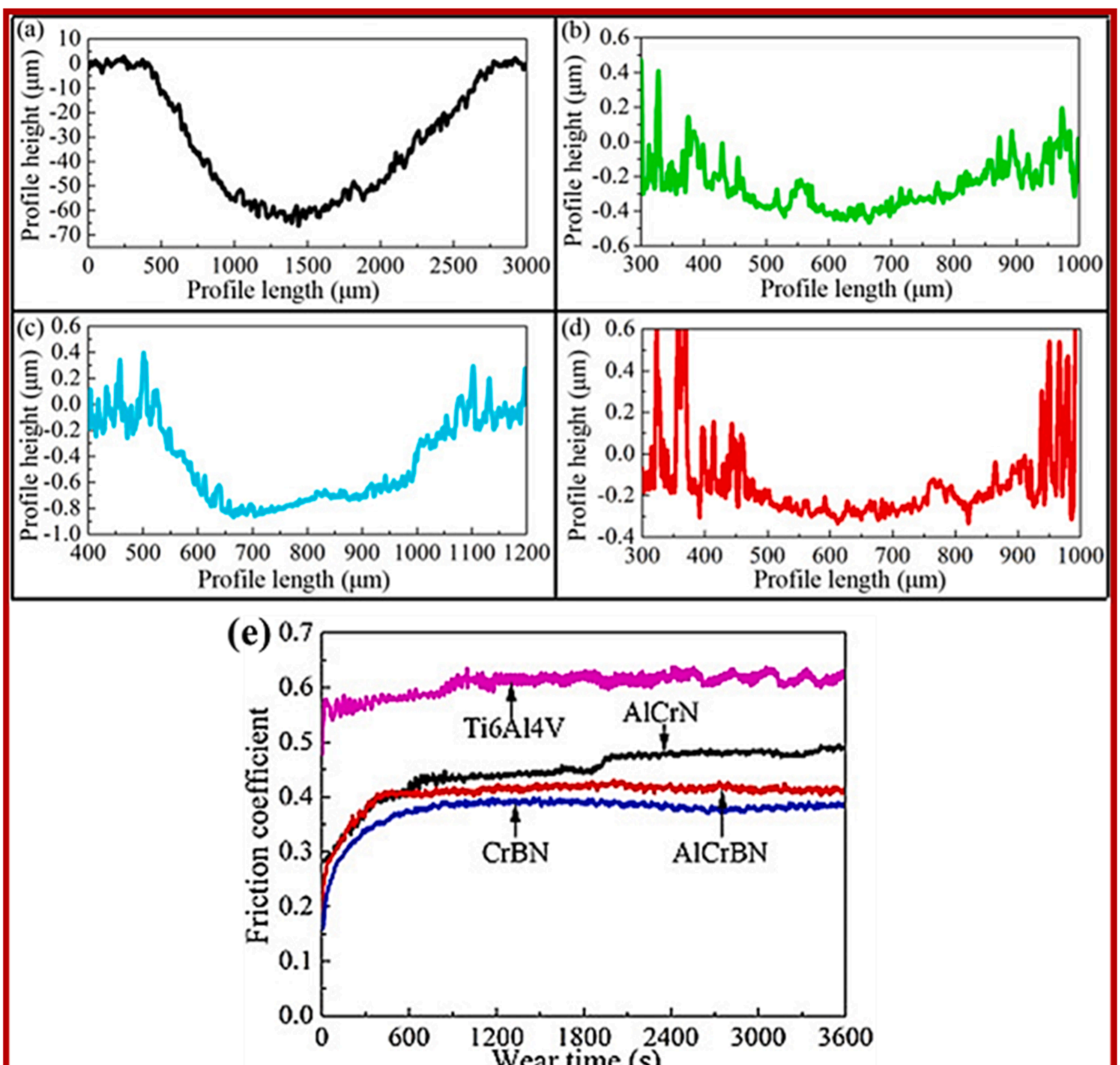

Fig. 9. Cross-sectional profiles of wear surfaces of uncoated and coated samples: (a) Ti6Al4V, (b) AlCrN, (c) CrBN, (d) AlCrBN, and (e) friction coefficients of uncoated and coated samples as a function of sliding time [113].

[94]. The friction coefficients for the uncoated Ti6Al4V surface, TiN, and TiSiN were approximately 0.15, 0.18, and 0.2, respectively. Notably, the wear rate of the TiSiN-coated surface with a silicon content of 17.2 wt% was measured at 2.5×10^{-15} m^3/N m. This value was approximately 10 times lower than that observed for the uncoated surface and three times lower than the wear rate associated with the TiN coating [94].

The wear surface profiles of the investigated materials sliding against a WC-Co ball under dry wear conditions are shown in Fig. 9(a-d), where it is evident that the AlCrN-, CrBN-, and AlCrBN-coated samples had much lower wear rates than the Ti6Al4V substrate. In comparison to the Ti6Al4V substrate, which had a wear rate of 1.6×10^{-3} $mm^3 \cdot N^{-1}$ m^{-1}, the wear rates were recorded at 2.35×10^{-6} $mm^3 \cdot N^{-1}$ m^{-1}, 4.93×10^{-6} $mm^3 \cdot N^{-1}$ m^{-1}, and 1.65×10^{-6} $mm^3 \cdot N^{-1}$ m^{-1}, respectively. This highlights the efficacious safeguard provided by PVD coatings, wherein the AlCrBN coating demonstrated exceptional anti-wear capabilities. Moreover, a significant decrease in friction was observed for the coated samples (0.45 for AlCrN, 0.37 for CrBN, and 0.4 for AlCrBN) in comparison with the Ti6Al4V alloy (0.6), as illustrated by the friction coefficient dynamics shown in Fig. 9(e). The outermost hard coatings of the samples, which have higher surface hardness and lower shear strength, are responsible for the reduced friction coefficients [113].

Additionally, in the work by Hatem et al. [95], the introduction of carbon atom doping demonstrated a significant reduction in the wear rate values upon applying the TiSiCN nanocomposite coating compared to the bare titanium surface. The wear rate ranged from 6.81×10^{-6} to 7.56×10^{-7} mm^3/N/m for the coated samples, whereas the uncoated titanium sample exhibited a wear rate of 2.61×10^{-4}. Among the coated samples, TiSiN exhibited the lowest wear rate, followed by TiSiCN. The exceptional tribocorrosion performance achieved by the high-carbon-content TiSiCN sample underscores the crucial role played by the self-solid lubrication capability inherent in the amorphous carbon regions within the coating structure. Moreover, Zhou et al. discovered that AlCrBN and CrBN nanocomposite coatings exhibited reduced friction coefficients [113].

The multilayer TiAlN coating reduced the wear rate and friction coefficient, while increasing the hardness and elastic modulus of the aluminum alloy surface. The TiAl and TiAlN layers alternate in the coating. For demanding applications, this coating offers better wear resistance and hardness than bare Al alloy, resulting in efficient surface protection [84]. Furthermore, three-multilayered systems with distinct crystal structures and lattice misfits Mo/Ni, TiN/Cu, and ZrN/W show special nanomechanical properties such as increased yield strength, softer elastic moduli, and a hardening effect [85]. In addition, studies on TiN/ZrN-coated nanotubular architectures on Ti–35Ta–xHf alloys for bio-implants seek to comprehend the ways in which these coatings impact surface characteristics to improve biocompatibility and durability, which could ultimately result in the creation of safer and more robust medical implants [86].

Comparable results were also observed for the coatings made of TiAlN and TiAlBN. All coatings displayed superior wear resistance compared to the standard TiN and TiAlN coatings. The most effective coating formulation consisted of 90% (Ti, Al) N and 10% BN, with an average grain size of 26 nm). The enhanced performance is attributed to the compliant a-BN phase, which allows for the displacement of (Ti, Al) N grains under load. This mechanism reduces the elastic modulus, increases the toughness, and ultimately improves wear resistance [117]. The existence of an amorphous structure is advantageous for improving wear resistance because amorphous structures lack grain boundaries (GBs). Consequently, there was no penetration of oxygen along the GBs, preventing oxidation reactions and reducing oxidation wear. The nitride coating exhibited strong bonding to the substrate, significantly enhancing both substrate hardness and resistance to plastic deformation. This improvement in material properties contributed to an overall enhancement in the bio-tribological performance.

3.1.3. Corrosion studies of MNs coated Ti6Al4V alloy

Metal-nitride coatings can significantly enhance the corrosion properties of bioimplants through various mechanisms. By incorporating metal nitride coatings, bioimplants can benefit from extended service life, reduced susceptibility to corrosion, and improved overall performance within the biological environment. These coatings contribute to the long-term success and reliability of bioimplants for medical applications. Using potentiodynamic polarization and open-circuit potential (OCP) in a simulated body fluid (SBF) solution, the corrosion behavior of untreated, TiN and TiAlN monolayer, and TiN/TiAlN multilayer films was examined. The OCP of the untreated β-type Ti45Nb substrate was measured at −0.337 V. After the TiAlN, TiN binary layer, and TiAlN/TiN multilayer coatings were deposited on the substrate, the corresponding OCPs rose to −0.247 V, −0.126 V, and −0.023 V respectively. During the first 15 min, the OCP values of the TiAlN- and TiN-coated samples decreased rapidly. However, they stabilized at these values, which were still higher than those of the untreated sample [118].

The corrosion behavior of the TiAlN-coated coatings and bare Ti6Al4V substrate are shown by the polarization curves in Fig. 10 (a) and (b). The TiAlN-coated Ti6Al4V samples had lower I_{corr} values (ranging from 59.740 to 2.135 $\mu A \cdot cm^{-2}$), showing superior corrosion resistance. Tafel plots derived from polarization curves provided valuable quantitative data regarding a material's corrosion behavior. By analyzing the slope of the Tafel lines, corrosion current (I_{corr}), potential at corrosion equilibrium (E_{corr}), and passivation region, one can evaluate and compare the corrosion resistance of different materials, as demonstrated in the provided information regarding the TiAlN-coated Ti6Al4V samples exhibiting lower I_{corr} values and superior corrosion resistance compared to the bare Ti6Al4V substrate [118,119].

The Nyquist plots (Fig. 10 (c) and (d)) show a higher global impedance (Z) for the TiAlN-coated sample, demonstrating its capacitive nature and superior corrosion protection. Electrochemical impedance spectroscopy (EIS) studies further clarified this phenomenon. The TiAlN-coated sample also had a greater phase angle and impedance, highlighting the fact that it is more capacitive than resistive and improves its resistance to corrosion. Fig. 10 (e) and (f) show a substantially larger impedance for the decorated surface. The research team discovered that the form and diameter of the capacitive loop in the Nyquist plot correlated with the charge transfer resistance (Rct), proving its outstanding corrosion resistance [119].

Furthermore, the corrosion current density of the multilayer coating was smaller than that of the untreated samples at 1.25×10^{-9}A. cm^{-2}, with a value of 53.9×10^{-9}A. cm^{-2}. Measuring 19.41 and 4.06×10^{-9}A. cm^{-2} are the corrosion current densities of the TiN and TiAlN monolayer coatings, respectively. Hee et al. [120] grain boundaries act as physical barriers against corrosion, and the size of crystallites has a substantial impact on how well coatings resist corrosion. A reduced crystallite size results in a higher density of grain boundaries, consequently lowering the corrosion rate within the microstructure compared to microstructures with larger crystallites. The microstructure featuring smaller crystallites in the multilayer film exhibited improved corrosion performance in titanium alloys owing to an increased number of physical barriers. This smaller crystallite size hindered the penetration of corrosive electrolytes into the substrate when compared to monolayer coatings. Titanium nitride coatings are commonly utilized as corrosion-resistant coatings in implant materials [120].

Noori et al. [121] used the cathodic-arc evaporation (CAE) physical vapor deposition (PVD) method to examine the structure, bioactivity, and corrosion resistance of two multilayer thin films deposited on Ti6Al4V. The coatings included single layers of ZrN and TiN for comparison as well as multilayer combinations of CrN, TiN, and CrN/ZrN with different layer topologies. The bioactivity and corrosion resistance of CrN/ZrN multilayer coatings were found to be promising, indicating their potential for biomedical applications.

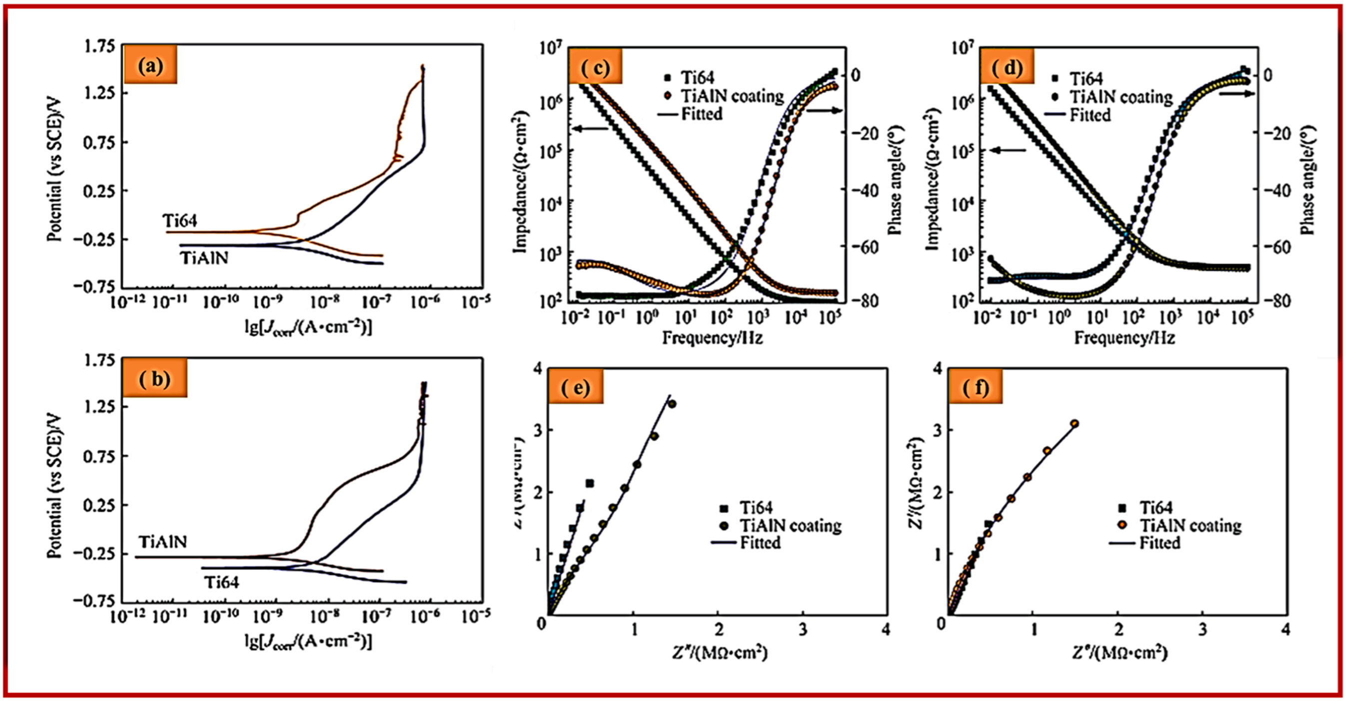

Fig. 10. shows Tafel plots comparing the uncoated Ti6Al4V and TiAlN-coated samples in artificial saliva (AS) (a) and simulated body fluid (SBF) (b). Bode plots for both coatings in SBF (c) and AS (d) media are depicted along with Nyquist plots in SBF (e) and AS (f) media [119].

3.1.4. Wetting property of MNs coated Ti6Al4V alloy

The wettability of a material significantly influences protein adsorption, and consequently, cell adhesion. Typically, biomaterial surfaces that exhibit moderate hydrophilicity enhance cell growth and demonstrate increased biocompatibility. Water contact angles (WCAs) were measured to assess the wettability of the TiN-coated surfaces. Both coated and uncoated samples showed a trend in which the contact angle (CA) values first declined and subsequently increased with increasing texture density, according to the study. In particular, compared to samples with nitride coating, where all CA values were higher than 90°, all uncoated sample CA values were less than 90°, suggesting higher hydrophilicity. This implies that the samples were made more hydrophobic by the nitride coating, which was particularly apparent in samples with comparable texture densities. The intimate connections between biological fluids and the hydrophilic surfaces of dental and orthopaedic implants enable normal protein adsorption and subsequent interactions with cell receptors, as presented in Fig. 11(A). Fig. 11(B), on the other hand, shows that hydrophobic surfaces can become contaminated with hydrocarbons. This can cause air bubbles to become trapped, which may impede protein adsorption and cell receptor adhesion/

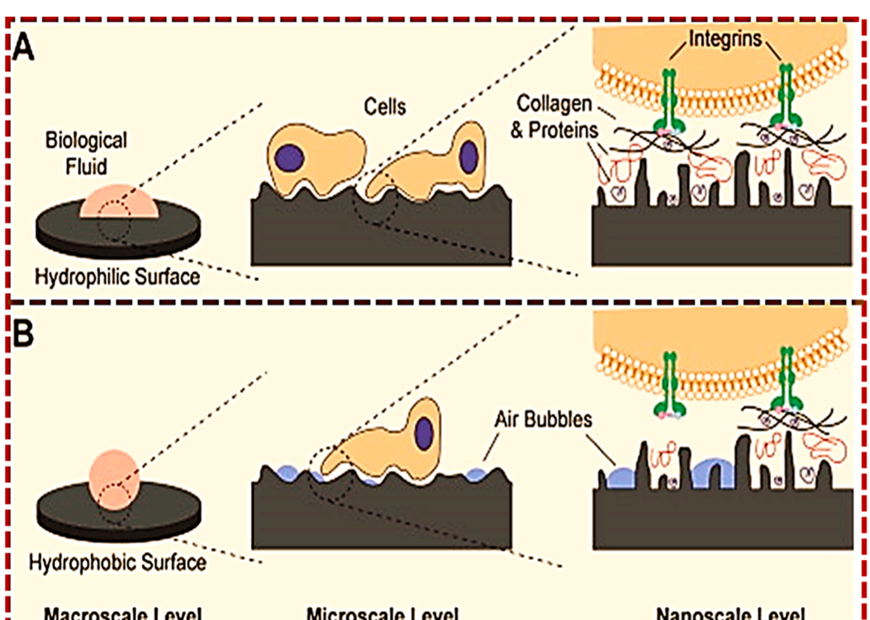

Fig. 11. provides a visual representation of the potential interactions occurring at various length scales with both hydrophilic (A) and hydrophobic (B) surfaces [125].

activation. However, developing a thorough implant design that promotes early and long-term osseointegration requires a better understanding of the function of surface wettability and its effect on the surrounding biological environment.

Moreover, the significant rise in contact angle (CA) values observed in the nitride-coated samples in comparison to the uncoated samples was mainly caused by the modification of surface chemical compositions brought about by the nitride coating's development. Furthermore, the microscale surface roughness was increased by the presence of worm-like strip nitrides [122]. TiN surface treatments, such as O_2 plasma treatment (TiN-O_2), acrylamide (AAm) polymer grafting (TiN-g), and bone morphogenetic protein 2 (BMP2) immobilization (TiN-g-BMP2), were evaluated in terms of their water contact angles (WCAs). The initial WCAs for untreated Ti6Al4V and TiN surfaces were $68.7 \pm 1.2^\circ$ and $73.2 \pm 0.8^\circ$, respectively. On the other hand, the WCA sharply decreased to less than 10° after O_2 plasma treatment (TiN-O_2), suggesting extremely high hydrophilicity on the TiN surface. Following the AAm grafting (TiN-g) and BMP2 immobilisation (TiN-g-BMP2), the TiN surface exhibited a minor hydrophobic shift, with WCAs of $36.4 \pm 1.7^\circ$ and $51.5 \pm 1.4^\circ$, respectively [123]. The potential of titanium nitride (TiN) coating on metal implants was investigated by Bai et al. They showed that surface oxidation via hydrothermal treatment efficiently increases the osteoconductivity of the material. On the prepared TiN-coated surface, the first contact angle of wetting varied between 92 °and 50.4°. The contact angle of distilled water (DW) on the TiN coated surface gradually decreased with increasing hydrothermal treatment temperature. This suggests that the wettability of TiN coatings can be enhanced by hydrothermal treatment [124].

3.1.5. Biocompatible properties of MNs coated Ti6Al4V alloy

The necessity of ensuring that materials are inserted into the body is not necessary because negative reactions are highlighted by the close proximity of biomaterials to living tissue. Therefore, bio-implant surfaces must be free of harmful substances and non-allergenic materials. Hard-coating biocompatibility is largely determined by biological evaluations, including cytotoxicity for tissue compatibility, hemocompatibility and hemolysis for blood compatibility, antibacterial activity to measure bactericidal effects through in vitro cell line studies, and in vivo animal studies. Antonio et al. investigated the in vivo antibacterial activity of titanium nitride applied to titanium surfaces [126]. In this study, six participants had removable acrylic devices, both uncoated and coated with titanium nitride (TiN) fixed to the molar-premolar region of their jaws. Scanning electron microscopy (SEM) analysis of the devices after a day showed a notable decrease in the amount of bacteria on the TiN-coated surfaces. Additionally, utilizing a variety of cell lines, including human bone marrow stem cells (BMSCs), the biocompatibility and cellular toxicity of the nitride coatings were examined in vitro [127]. Researchers [128] conducted studies involving various cell types, including Sarcoma osteogenic (Saos-2) cells, osteoblast-like cells, mouse fibroblasts, human fetal osteoblasts, murine calvarial osteoblasts, and murine monocyte cells. Cytotoxicity evaluations across various cell lines demonstrated superior cell viability and proliferation on the nitride coating compared with the control samples. Additionally, nitride coatings demonstrated remarkable cell adhesion, maintaining the natural morphology of live cells while stimulating cell differentiation and metabolic function [96].

Brunello et al. compared fibroblast proliferation and bacterial biofilm inactivation of TiN and ZrN coatings [129]. Immunofluorescence (IF) staining of vinculin highlighted its role in forming essential adhesions, indicating strong connections between cells. Moreover, the actin cytoskeleton emphasizes cell adherence to the surfaces, suggesting that the TiN and ZrN coatings interact well with one another. The coatings exhibited remarkable bactericidal activity against five distinct types of bacteria, indicating their effectiveness in averting bacterial colonization and infection. Tantalum nitride (TaN) was shown to be biocompatible by Li et al. [130] using bone marrow stem cells (BMSCs). Images showed that enlarged BMSCs had a typical spindle-shaped morphology, which indicates that cell adherence and spreading on TaN coatings were successful and occurred more quickly than in the control samples. The differentiation of cells involved in osteogenesis determines the biological effectiveness of orthopaedic implants. The main measure of osteoblast function and differentiation is alkaline phosphatase (ALP) activity, which is directly correlated with osteoblastic activity [131]. Calcium nodules are mineralized from the extracellular matrix (ECM) during later phases of osteogenesis. As a result, calcium deposition acts as an indication of osteogenesis, and alizarin red staining was used to measure it [131].

Examining the effect of surface texture and nitride coating on cyto-biocompatibility followed experiments that verified the enhanced wear resistance. Initially, to separate the impact of the coating on MC3T3-E1 cell adherence and spreading, samples with and without nitride coating were selected. Fluorescence microscopy images of the samples over 1, 3, and 7 days were shown in Fig. 12. After a day, the cells spread evenly across the uncoated and nitride-coated samples and displayed a spindle-shaped morphology. In both samples, the number of cells increased by the third day, and the cell appearance became flatter. Seven days later, there was an increase in pseudopodia and overlapping development in the cell spreading zones on both surfaces. The nitride covering and Ti6Al4V substrate both produced ideal chemical and physical conditions for MC3T3-E1 cell adhesion and proliferation, as demonstrated by laser confocal imaging [132].

TiCrN and TiN coated Ti6Al4V, which were synthesised using the SLM process, showed antibacterial characteristics (>50%), good biocompatibility, and noncytotoxicity in in vitro studies. According to Ni et al.'s research, these results imply that TiCrN and TiN coated SLM Ti6Al4V have potential benefits for use as femoral components in orthopaedic implants [112]. For example, Nikolova et al. [133] Electron Beam Melting (EBM) is effective in both enhancing the surface hardness and inducing consistent surface roughness in the Ti6Al4V alloy. Following the application of a 3.7 μm thick TiN/TiO_2 film through physical vapor deposition, the implant surfaces of the modified alloy exhibited robust bonding strength and excellent bioactivity. Hybrid surface treatment, devoid of cytotoxicity, presents a potential advantage for enhancing the osseointegration of dental or orthopedic implants.

3.1.6. The effect of MNs coating thickness on the resulting properties

The thickness of MNs coatings plays a crucial role in determining their resulting properties, impacting both their mechanical and biological performance. In the study by Kazemi et al. [134], the incorporation of a dual-layer HA/TiN coating on Ti6Al4V implants significantly influenced corrosion resistance and biocompatibility. A thicker HA/TiN coating led to higher roughness, resembling bone structure and promoting cell growth, thereby enhancing biocompatibility. Moreover, the increased thickness of the deposited film contributed to lower corrosion current density, indicative of improved corrosion resistance. Additional, the study [135] of TiN and PN layers were found to have thicknesses of 2.1 μm and 0.9 μm, respectively, contributing to a total bilayer thickness of approximately 4.3 μm. Despite variations in coating factors such as temperature and electrolyte content, electrochemical tests revealed excellent corrosion resistance for all coated samples, with the PN/TiN double layer exhibiting superior performance.

Similarly, in the investigation by Zhao et al. [122], changes in the film thickness of 2.4 μm for the TiN layer and 3.6 μm for the diffusion layer. This alteration in film thickness was instrumental in achieving a significant increase in substrate hardness, elevating it from 1.7 GPa to 8.6 GPa. Comparative analysis revealed that coated samples displayed reduced average frictional coefficients and wear rates in comparison to uncoated samples, decreasing from 0.34 and 18.27×10^{-6} mm^3/N·m to 0.29 and 0.33×10^{-6} mm^3/N·m, respectively. Consequently, the impact of the Ti6Al4V alloy substrate on the measured nanomechanical characteristics of TiN coatings was taken into consideration, since cathodic arc produced nitride coatings accounted for less than 10% of the TiN

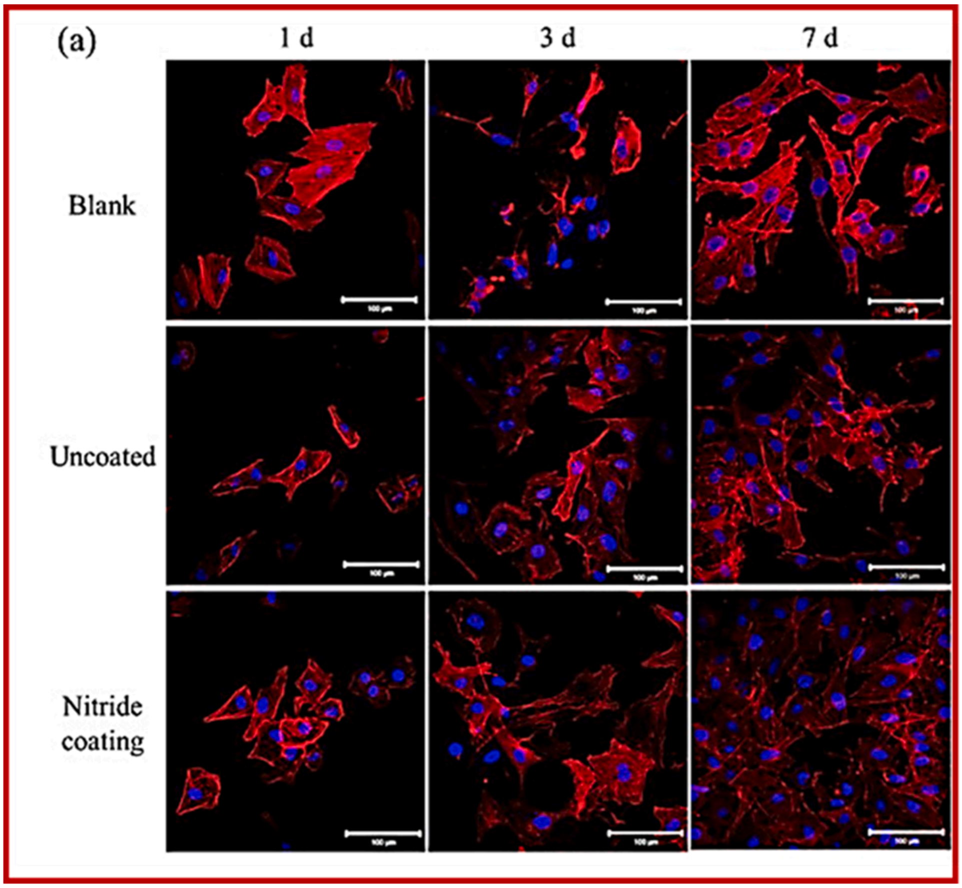

Fig. 12. displays rhodamine-phalloidin and DAPI-stained immunofluorescence pictures of MC3T3-E1 cells co-cultured with materials that had no surface roughness (texture density of 0) at 1, 3, and 7 days [132].

coating thickness (3.0 ± 0.1 μm). The coatings showed high Young's modulus (458.4 ± 79 GPa) and hardness (33.4 ± 10 GPa), and adhesive failure was revealed at 2.9 ± 0.3 GPa in scratch testing. Against an Al_2O_3 ball, the intrinsic in vitro wear rate was $6.8 \pm 1.7 \times 10^{-7}$ $mm^3/N{\cdot}m$. A wear rate of $1.9 \pm 0.7 \times 10^{-5}$ $mm^3/N{\cdot}m$ was observed in testing against ultrahigh molecular weight polyethylene, indicating better performance than the CoCrMo alloy. The coatings' superior cell-interaction capabilities and non-toxic nature were validated using in vitro biocompatibility evaluations employing the NIH3T3 cell line [136]. The thickness data compiled in Table S1 of the supplementary file provides a comprehensive overview of various standard nitride coatings reported in literature and studies, specifically focusing on their mechanical, wetting, tribological, and biocompatible applications.

Table 3 shows the numerous standard nitride coating deposition techniques used in the technical literature and studies of mechanical, wetting, tribological, and biocompatible applications. Biocompatible nitride coatings exhibit excellent biocompatibility in both blood and bone tissues, as evidenced in previous studies (Table 3). Furthermore, they possess favorable mechanical, tribological, and anticorrosion properties. Thus, ternary titanium nitride coatings are the most suitable choice for safeguarding the surfaces of medical implants.

3.2. Diamond-like carbon (DLC) biocompatible coatings

Hydrocarbon coatings, such as diamond-like carbon (DLC), are recognized for their impermeability and inertness, which qualify them for use in biomedical settings, especially orthopaedic implants. DLC coatings have a variety of applications in orthopaedics, cardiovascular components, and guidewires, owing to their remarkable hardness, low friction, and complete biocompatibility. The significance of cautious application in maximizing the performance has been highlighted in a recent study. Superior tribological and mechanical qualities, as well as resistance to corrosion, hemocompatibility, and biocompatibility, place DLC in a promising position for biomedical applications [146]. orthopaedics, dentistry, and cardiovasculars use DLC films with a variety of atomic bond compositions and configurations. No cytotoxicity or inflammatory reactions were observed when the cells were integrated onto the DLC coatings. DLC coatings have demonstrated efficacy in orthopaedic applications by mitigating wear, corrosion, and debris production. Furthermore, they demonstrate a reduced thrombogenic response through the reduction of platelet adhesion and activation [147]. A wide range of cutting-edge diamond-like coatings is shown in Fig. 13, demonstrating their important function in surface modification for Ti6Al4V orthopaedic bio implants. Especially in the harsh biomechanical environment of the human body, these coatings offer a state-of-the-art method of enhancing the functionality and longevity of orthopaedic implants.

DLC is a perfect base coat for alloying with different elements. Because of its amorphous nature, additional elements, such as W, Si, Mo, N, F, V, O, Co, Ti, and their combinations, can be incorporated into the coating without affecting its amorphous phase. This technique allows for the constant modification of a variety of film properties to satisfy specific requirements, including tribological traits, electrical conductivity, surface energy, and cellular biological processes. DLC is now used in two main biological domains: reducing wear in load-bearing joints and blood-contacting devices like heart valves and stents. Although commercially accessible heart valves and stents coated with DLC are widely available, the status of DLC-coated load-bearing implants is yet unknown. To gain an introduction to DLC, readers are encouraged to refer to the review articles authored by Robertson [148,149] and Butter

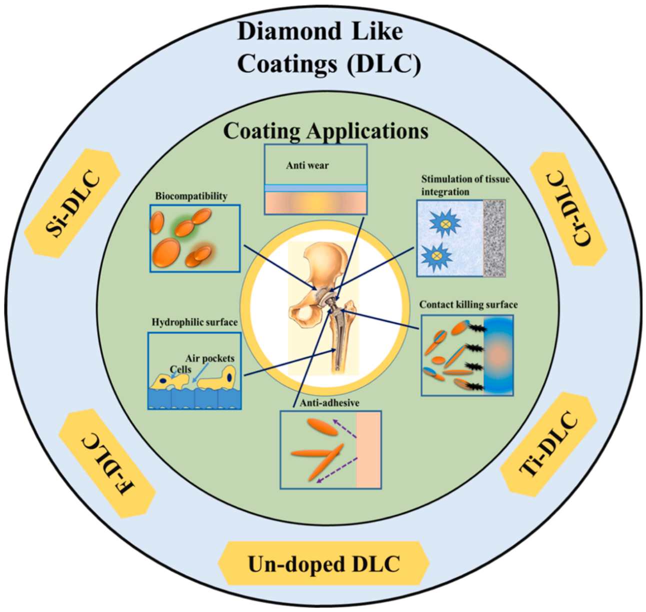

Fig. 13. Different advanced DLC and composite of DLC coatings employed for modifying the surface of Ti6Al4V orthopedic bio implants and their applications in various biomedical settings.

and Lettington [150]. These articles offer comprehensive insights into the properties, synthesis methods, and applications of DLC, serving as valuable resources for understanding this versatile material.

3.2.1. Mechanical properties of DLC coated Ti6Al4V alloy

For many biomedical applications, it is crucial to keep friction and wear rates low while making sure that the hardness of the coating doesn't overwear the opposing material. Experiments and computer simulations, especially molecular dynamics modelling, have shown that the outer layers of DLC change into graphite under sliding wear conditions, with their basal plane aligned parallel to the surface. This phenomenon offers important insights into the behavior of DLC coatings under mechanical stress, which is essential for understanding the durability and performance of these coatings in practical applications. According to Liu et al., this transition enables facile shearing at load-bearing asperities, leading to extremely low friction and wear rates [151]. Generally, a monomolecular layer of hydrogen is applied to surfaces, regardless of whether they are composed of graphite or diamond. This layer lowers the adhesion to the counterfaces, especially when the contact pressure is as high as 1 GPa. The potential advantages of employing metal components coated with DLC for biomedical implants, notably total hip and knee replacements, are evaluated in this review. DLC coatings offer low-friction, long-lasting, inert, and wear-resistant surface options to improve implant performance. This study critically evaluates previous studies in this field, emphasizing achievements and shortcomings and pinpointing areas where DLC-coated metal components should be improved to achieve the best performance in the human body. It also examines the current developments in the composition and deposition methods of DLC coatings for the creation of implants in the future.

Researcher Ding et. al. [152] using a fretting-wear testing apparatus, the study examined the frictional behaviour of the DLC covering and Ti6Al4V alloy under fretting circumstances. The nanohardness and elastic modulus of the DLC coating were greater than those of the Ti6Al4V matrix. Consequently, the average friction coefficients were rather high at approximately 0.5. Peng et al. investigated the impact of post-deposition treatments and the surface roughness of DLC coatings created using three different processes [153]. The chosen techniques for coating deposition include DC magnetron sputtering in argon, RF plasma-activated CVD in methane, and utilizing a carbon ion beam generated by a cathodic arc discharge. Each technique allows for variation in the bias voltage applied to the substrate, with the capability to adjust it up to approximately 350 V. These methods offer flexibility and control over the coating process, enabling precise tuning of parameters to achieve desired coating properties and characteristics for specific applications. Some samples were heat treated at 500 °C in a vacuum, hydrogen etched in a plasma, or sputter-deposited in an argon plasma after deposition. The silicon substrates were purified by argon sputtering and had a surface roughness of only 0.046 nm [154]. Therefore, under ideal circumstances, DLC coatings as thick as 700 nm may display a level of smoothness similar to that of meticulously manufactured silicon crystal substrates, which is extremely beneficial for orthopaedic applications. Moreover, a tribofilm was seen to form on the Ti6Al4V surface sliding against a DLC coating when fretting conditions were applied in air. The lower Young's modulus was approximately 1.3 times greater than that of the alloy, according to nano-indentation tests, which also showed that its hardness was 2.6 times higher than that of Ti6Al4V alloys [155].

3.2.2. Tribological properties of DLC coated Ti6Al4V

Within the field of biomedical applications, there are two main areas for intensive research on DLC films. To minimize platelet adhesion and activation, DLC was first investigated in blood-contacting applications to reduce thrombus formation. Second, DLC is used in load-bearing situations, especially in articulated implants, where its strong wear resistance, low coefficient of friction, and superior hardness reduce wear and extend the life of orthopaedic implants and other precision components [156]. Although there have been great developments in the field of DLC-based materials, there are still certain limitations with regard to their biocompatibility. Total joint replacement (TJR) is a common medical treatment that requires implants to stay within the body for long periods of time. This emphasises how crucial it is for implants to have outstanding bio-tribological qualities and be biologically compatible with host tissues in order to prolong their lifespan [157]. The main reasons for total joint replacement (TJR) failure are osteolysis brought on by wear, loosening, stiffness, and instability, as well as infection. It became clear that titanium alloys were inappropriate for bearing surface applications without the proper coating or surface treatment when it was recognized that these alloys had insufficient wear resistance. As a result, using a DLC film became a practical way to protect implants made of titanium [158] [159].

Specifically, the COF decreased from 0.452 to 0.413 under dry sliding conditions and from 0.228 to 0.197 when lubricated with 25% bovine serum. This reduction in COF indicates an improvement in the tribological performance of the samples following thermal oxidation treatment, suggesting enhanced surface properties and lubrication capabilities. On the other hand, the original samples average COF was decreased to 0.083 in dry sliding and to 0.108 with 25% bovine serum lubrication upon applying the DLC treatment via spraying [160]. Wang et al. [161] researchers found that the friction coefficients of fluorine-doped diamond-like carbon (F-DLC) sheets varied from 0.16 to 0.5 when the fluorine content was changed. All films did, however, ultimately achieve a low friction value between 0.05 and 0.21 during tribometry tests. They also observed a relationship between fluorine content and friction, with friction reducing as fluorine concentration rose. Furthermore, it was discovered that the wear rate decreased as the fluorine level in the F-DLC film increased. The film with 16.3% fluorine had the lowest wear rate, measured at 1.2×10^{-7} mm^3/Nm.

Fernando et al. [162] suggested that including a DLC film into dental tribosystems may have certain disadvantages, such as increased fracture vulnerability because of the films intrinsic brittleness and worse bonding between the film and substrate. On the other hand, these issues might be resolved by adding the right interlayers or dopants to improve the binding between the film and the substrate, as well as by designing the films characteristics to lower micro-contact stress and diminish fracture risk. Amanov and Sasaki [163] showed that using a combination of DLC-coated micro-dimples on a Ti64 substrate with oil lubrication could significantly reduce friction and wear rate. Nevertheless, this combination has not yet been assessed in the "conformal contact" scenario that is typical of prosthetic hip joints.

3.2.3. Corrosion properties of DLC coated Ti6Al4V alloy

To evaluate the corrosion properties of Ti6Al4V coated with biocompatible DLC (Diamond-Like Carbon). This entails researching the effects of the DLC coating on the alloy's ability to withstand corrosion in several settings. In order to protect implant material from corrosive effects of body fluids in biomedical applications, it is important to determine whether the DLC coating offers good corrosion protection. Scientists hope to guarantee the long-term robustness and dependability of medical implants by examining the corrosion behaviour of DLC-coated Ti6Al4V, which would ultimately enhance patient outcomes and safety. These coatings serve as an effective method for enhancing the surface properties of titanium alloys, particularly in biomedical applications where durability and biocompatibility are crucial factors [164] [147].

DLC coatings provide a way to mitigate Ti64's susceptibility to corrosion in various settings. Its corrosion resistance has been improved by surface treatment techniques, which has led to a number of studies looking into how surface coatings affect Ti64 alloys' electrochemical behavior [165]. Researcher, Arslan et. al. [166] comparison to the Ti6Al4V substrates, the Ti-DLC coatings showed a greater corrosion potential, indicating superior corrosion resistance. However, the corrosion current density (I_{corr}) of the Ti-DLC coatings was less than that of the Ti6Al4V substrate, indicating a decreased sensitivity to corrosion. These results show that the Ti-DLC coating works well in tribocorrosion and corrosive environments while providing good protection for the Ti64 alloy. The open circuit potential (OCP) values for the Ti64 substrate and Ti-DLC protective coatings during tribocorrosion experiments were −330 V and −560 V, respectively. This suggests that by serving as a barrier layer, the protective coating on Ti64 substrates improves tribocorrosion resistance.

Furthermore, the impact of adhesive interlayers of titanium or chromium on the interplay between DLC coated titanium and Ti64 in a physiological saline solution with lowered pH and fluoride ions added was investigated. Regardless of substrate type, both coated systems behaved similarly in a fluoride-ion-free environment. Specimens with a chromium interlayer displayed the best corrosion resistance for both types of substrates. However, coatings on Ti64 with an interlayer of titanium showed greater resistance to corrosion than those on titanium. Biological studies have indicated the suitability of a chromium interlayer for DLC-coated dental implants [165]. Furthermore, the addition of nanodiamonds can enhance the adherence of DLC and N-DLC on Ti alloy substrates, whereas a small amount of nitrogen doping can reduce the internal stress and surface roughness of the DLC films. Consequently, the films made of nano-diamond (ND)/ND/N-DLC showed the maximum corrosion resistance. On the other hand, ND/DLC films exhibit worse corrosion resistance than DLC films, whereas DLC films on bare Ti alloys demonstrate the lowest corrosion resistance [167].

3.2.4. Wetting properties of DLC coated Ti6Al4V alloy

Numerous studies have assessed the wettability and surface energy of DLC or DLC films with integrated components on Ti64 alloys and examined their hemocompatibility. The high free energy of the Ti64 substrate surface is necessary for effective coating adherence. Therefore, using characteristics including contact angle, roughness, elastic modulus, and Vickers hardness, researchers examined four surface treatments to see how they affected the wettability of the Ti64 substrate surface. The free energy of the Ti64 substrate surface is increased by both the texturing and carburizing treatments, with the combination treatment working best, according to the findings. Moreover, the surface roughness of the Ti64 substrate is significantly improved by both texturing and carburizing treatments, which is essential for strengthening the bonding between the substrate and DLC coatings [168].

Furthermore, untreated Ti64 samples showed similar water wettability, with contact angles of 65° for horizontally printed samples and 63° for vertically printed samples, respectively. However, depending on which way the samples were printed, the wettability of the DLC-coated samples varied significantly: the horizontal DLC-Ti64 sample had a contact angle of 38°, while the vertical DLC-Ti64 sample had a contact angle of 86°. As such, a surface that is highly wettable (between 60 and 65°) is designed to promote the best possible cell attachment and growth [169]. The DLC-coated Ti6Al4V surface showed clear variations in contact angle; the more wettable DLC-Ti6Al4V(H) surface had a contact angle of 38°, whilst the DLC-Ti6Al4V(V) surface had a greater contact angle of 86°. These variations in contact angle suggested variations in surface wettability and free energy. These physicochemical changes have an impact on the biological reaction seen in bone cell in vitro experiments. Comparing the planar TCPS control and the DLC-Ti6Al4V(H) surface to the DLC-Ti6Al4V(V) surface over a 7-day period, cell tests showed that the latter supported lower levels of cell growth. This implies that the vertical (V) surface features, which are comparatively hydrophobic and somewhat rougher, would be more favorable for the formation of bone cells [170].

Applying DLC coating improved surface roughness, wettability, and graphitic properties all of which are beneficial for long-term hip implant applications, as Kashyap et al. [74] found. Foetal bovine serum and deionized water were used to test wettability, and the results showed hydrophilic behaviour on all DLC-coated surfaces. In particular, when exposed to DI water, the Plain+DLC and HT+DLC surfaces showed a modest decrease in contact angle. The tribological performance was eventually improved by the combination of surface treatments, such as heat treatment, DLC coating, and low-temperature sulfurizing, which improved the wettability and lubricity at the interface during articulation.

3.2.5. Biocompatibility of DLC coated Ti6Al4V alloy

The practicality of DLC as a coating for in vivo uses depends on its established biocompatibility, which is confirmed by every study conducted to date. Lactate dehydrogenase (LDH) levels were used by Thomson et al. to measure the viability of DLC cells generated by the dual-beam ion method. The research was conducted using mice peritoneal macrophages and mouse fibroblasts. Their results demonstrated no harmful effects, proving the DLC coatings' biocompatibility [171]. Similar studies were carried out by Allen et al. using DLC produced by plasma-activated CVD and the murine macrophage cell line IC-21 in a growth medium supplemented with calf serum. Human synovial fibroblasts and the "osteoblast-like" human cell line SaOS-2 were used to measure cell proliferation. Counting was done 24 hours after disaggregation and staining to assess the growth kinetics of the cells during each incubation period. This method made it possible to thoroughly investigate the kinetics of cell growth and how the DLC coating affects it. On DLC-coated glass and polystyrene substrates, the results showed vigorous cell proliferation without aberrant morphology. Moreover, on DLC surfaces, cells showed increased filopodia formation, robust adherence, and quicker development [172].

Additionally, when compared to untreated Ti64 samples, DLC-coated samples showed a notable improvement in corrosion resistance. The coatings produced with a 30 W bias power produced lower cluster sizes and showed very slight changes to the surface morphology of the substrate. With a corrosion current of 6.47 nA/cm^2 and a corrosion rate of 8.05 nm/year, these coatings showed the lowest results, around 30 times lower than those coated at 60 W bias power and 47 times lower than untreated samples. Furthermore, assessments from in vitro cell culturing tests demonstrated the highest level of biocompatibility, indicating that the a-C coating might encourage tissue repair around the implants [173].

Researcher, Yick et al.[168], discovered that advancements in 3D printing technology have made it easier to create custom implants called extra low interstitials. These implants can now fit people's body parts more accurately because they're made to match the unique shapes of each person's body. To investigate possible enhancements in their biological characteristics, Ti64 ELI samples were printed in two directions using an electron beam melt process and then coated with diamond-like carbon (DLC). Based on the printing direction, the wettability of DLC-coated materials varies significantly; for example, DLC-Ti64 exhibits a contact angle of 86°, whereas DLC-coated Ti64 exhibits a contact angle of 38°. Using Saos-2 osteosarcoma cells, in vitro investigations are conducted to investigate the effects of surface chemistry and shape on the bioactivities of coated and uncoated samples. Even though DLC-coated surfaces passed good biocompatibility testing, more in vivo studies are required to confirm these findings.

Moreover, Xu and Pruitt examined in pin-on-disk tests against ultra-high molecular weight polyethylene (UHMWPE) the biocompatibility of DLC coatings on Ti6Al4V alloy. Using osteoarthritis-oriented synovial fluid (OASF), which contains all key biological components in optimal concentration ratios, Ghosh et al. DLC-coated Ti6Al4V in bio-tribological experiments, concentrating on the advanced interface of hip joints. If a DLC-coated micro-dimple interface is successfully implemented, fretting wear problems may be reduced by providing a single part for the stem and head instead of a tapering joint [174] [175].

Researcher Kashyap et al. [74] The bio-tribological performance of the improved surface was evaluated by simulating hip implant articulation using an elliptical sliding contact. Increased surface roughness, well wettability, and improved graphitic properties were demonstrated by DLC coating that had undergone prior heat treatment. Along with better adhesion strength, deformation resistance, and appropriateness for hip implant applications, the heat treatment also promoted the development of Cr_2O_3 and TiO_2 phases. Table 4 summarizes the possible advantages of employing DLC-coated Ti6Al4V materials, taking into account substrate-coating combination, deposition method, coating characteristics, and biocompatibility.

3.2.6. The effect of DLC coating thickness on the properties

Increasing DLC coating thickness generally leads to higher hardness values, providing improved resistance against mechanical wear, which is beneficial for applications like cutting tools, automotive components, and medical implants. Thicker DLC coatings also offer superior wear resistance by providing a thicker protective layer against abrasive wear, extending component lifespan in applications involving sliding or rubbing contact, such as gears, bearings, and mechanical seals. While DLC coatings inherently provide excellent corrosion resistance, thicker coatings may offer slightly better protection against corrosive agents due to their thicker barrier [76]. Additionally, DLC coatings exhibit consistent low wettability properties, desirable for applications requiring reduced friction and resistance to moisture or liquid ingress, such as medical devices and fluid handling systems. In biomedical applications, thicker DLC coatings can potentially enhance biocompatibility by providing a more robust barrier between the substrate and the biological environment, though thorough testing is necessary to ensure compliance with specific requirements. Overall, careful consideration of coating thickness alongside other parameters is essential to optimize DLC coatings for various applications, ensuring desired mechanical, protective, and biocompatible properties [76].

Sahoo et al.[176] studied, DLC coating thickness increases the edge radius of the micro tools, which may result in adverse rubbing and plowing that need to be investigated. In this work, DLC coatings of 440, 640, and 1160 nm thicknesses with a ~250 nm Cr interlayer are deposited on WC micro-end mills using a cathodic-arc system. DLC-coated surfaces exhibited enhanced tribological and mechanical properties compared to uncoated surfaces. The DLC-640 coated tools exhibit a reduction of ~ 40.51% in edge radius, ~45% in cutting forces, ~50.43% in surface roughness, and ~56.02% in burr height as compared to an uncoated tool. Hence, under the conditions investigated, it can be inferred that DLC-640 coating is the optimal coating choice, as it has an adequate thickness to resist wear, and the edge radius is not large enough to let the plowing phenomenon offset the beneficial effects of enhanced lubrication and abrasion resistance.

Although, under the chosen processing parameters a DLC thickness of between 0.7 and 3.0 μm has an influence on the structure, surface morphology and cohesive damage, no effect on the adherence and resistance against abrasive wear were found. The DLC reveals a good adherence to the titanium-alloy and coating spallation at the scratch edges was detected at about 35 N during the scratch test for all coating thickness. The susceptibility against cohesive damage also is of outstanding interest for the biological acceptance of the DLC. The results from the scratch tests mark the 0.7 μm thick DLC as the most suitable coating [147]. Moreover, Table S2 in the supplementary file offers a detailed compilation of thickness data pertaining to a wide range of standard DLC coatings as documented in literature and research studies. This compilation is specifically geared towards understanding the applications of these coatings in mechanical, wetting, tribological, and biocompatible scenarios.

The use of DLC coatings in the in vivo bearing interfaces of artificial joints has been demonstrated to improve implant performance and prolong usable life by lowering friction, wear rates, and increasing

Table 4
Previous studies have synthesized findings on nanostructured DLC coating properties on both AM and commercially available Ti6Al4V substrates.

DLC coatings	Coating Techniques	Mechanical wetting Properties	Wear and Corrosion Properties	Biocompatible coatings	Ref.
DLC coatings	Magnetron sputtering	20.4 GPa	COF=(0.06–0.08), -440 mV	Biomedical applications	[36]
Silver-doped DLC	Plasma reactor CVD technique	70–76°	-	Promoted faster bio-integration	[177]
DLC coatings	PA-CVD-deposition	13.7–26 GPa	COF=(0.033–0.120)	Hip joint bearing	[75]
DLC and Ti doped DLC coatings	Cathodic arc evaporation	8–22 GPA	COF= (0.202–0.172), (0.25–9.03) $\times 10^3$ mm^3	Biomedical applications	[178]
DLC coating	Magnetron sputtering	-	Wear Rate= 9.77×10^{-9} mm^3/N.m	Artificial hip joints	[178]
Fluorine doped DLC)	Cathode plasma immersion ion implantation	10.3–18.3 GPa	COF= (0.11–0.18) Wear rate = 9.77×10^{-7} mm^3/N.m	Biomedical applications	[161]
DLC and Si interlayer	Plasma enhanced chemical vapor deposition	98.7 °	-	Blood compatibility	[179]
Si-DLC	Plasma Enhanced Radio Frequency Chemical Vapour Deposition	16 GPa, 62.6 °	-	Antibacterial properties	[180]
Cr doped DLC	Magnetron sputtering	19.55–21.22 GPa,	E_{corr}= (-0.16) V I_{corr}= 2.10×10^{-8}A/cm^2	Biomedical applications	[181]
DLC coatings	Laser surface texturing	2093–2184 HV, 40.12–65.74°	-	Hip implant	[74]

wetting properties, according to the analysis from the table data. By offering improved wear resistance and robust antibacterial capabilities, multifunctional DLC coatings doped with bioactive elements like copper (Cu) and silver (Ag) have great promise to advance the next generation of load-bearing medical implants. Attempts to put Cu or Ag doped DLC coatings on polyethylene (PE) surfaces have been rather rare thus far. However, since DLC applied to PE has shown outstanding wear behavior, DLC surface alterations seem promising [182].

As such, Cu ions have been identified as having remarkable antibacterial qualities in Cu-doped DLC coatings, all the while being biocompatible coating additives. The difficulty of implanting Cu onto hard surfaces, such titanium, is a major disadvantage despite these benefits. Cu's poor solubility in ethanol-based solutions presents a problem because it makes it impossible to assemble high-dosage colloidal solutions for dip coating. In addition, Cu has a propensity to aggregate in polyvinylpyrrolidone matrix, which presents challenges for the production of DLC-coated joint prosthesis [182,183].

3.3. High entropy alloy (HEA) biocompatible coatings

A novel class of materials known as high entropy alloys (HEAs) is composed of at least five primary metallic elements that have compositions that are equiatomic or nearly equiatomic. HEAs are notable for surface modification and coating because of their exceptional resistance to corrosion, wear, high strength and hardness, and strong diffusion resistance. Because HEAs can incorporate customized excellent biocompatibility, surface topography, appropriate surface chemistry and customised element composition design, they are becoming more and more recognised as a viable choice for biomedical applications [37]. It is important to separate the coating process from other physicochemical surface treatments done on metallic biomaterials. Because of their unique qualities and ability to be used in a variety of environmental settings, HEA-based coating materials have become popular high-performance alternatives. As a result, since their discovery in 2004, research and development on HEA-based coating materials have progressed quickly [184].

In order to solve problems such as intrinsic bio-inertness, possible corrosion, and inadequate surface qualities, metallic biomaterials frequently require coating and surface changes. Because of its ability to combine customized surface topography, improved biocompatibility, appropriate surface chemistry, and tailored element content, HEAs have become attractive candidates for biomedical applications. In comparison to commercially available Ti6Al4V, this discussion assesses the mechanical, corrosion, and biocompatibility qualities necessary for HEAs in biomedical applications [185]. The manufacturing processes for HEA-based coatings can be broadly classified into the following categories, as shown in Fig. 14; (i) Vapour deposition techniques, such as vacuum arc deposition and magnetron sputtering; (ii) laser-based techniques, such as laser surface cladding, laser deposition, laser surface alloying, and plasma cladding; (iii) Thermal spraying techniques, which include high-velocity, plasma spraying, oxygen-fuel spraying, and cold spraying [37].

Several high entropy alloy coatings are shown in Fig. 15 to illustrate their important function in surface modification of Ti6Al4V orthopaedic bio implants. These coatings are a state-of-the-art method to improve orthopaedic implants' longevity and performance, particularly in the harsh biomechanical environment of the human body. These high entropy alloy coatings play a significant role in the success and dependability of orthopaedic implantation procedures by successfully modifying the surface properties of Ti6Al4V implants, such as increasing mechanical strength and resistance to corrosion.

3.3.1. Mechanical properties of HEA coated Ti6Al4V alloy

Hardness, compression, tension, fatigue, serration behaviour, and nanoindentation are just a few of the mechanical properties of HEAs that

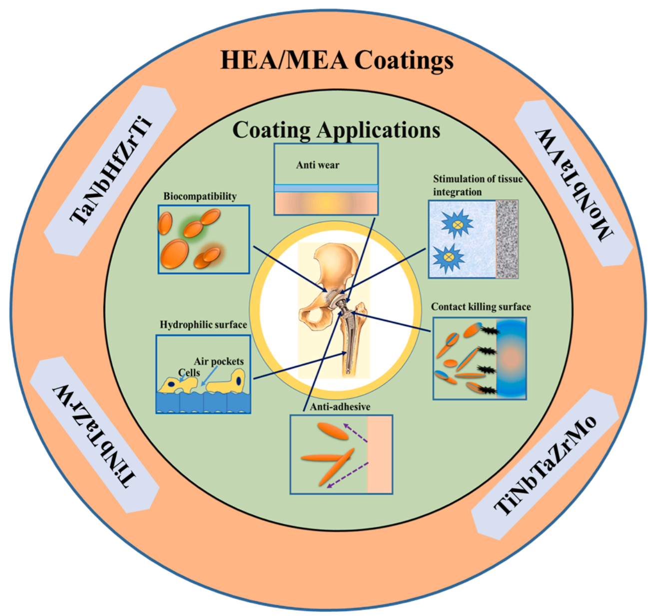

Fig. 15. Different advanced medium/high entropy alloy coatings employed for modifying the surface of Ti6Al4V orthopedic bio implants and their applications in various biomedical settings.

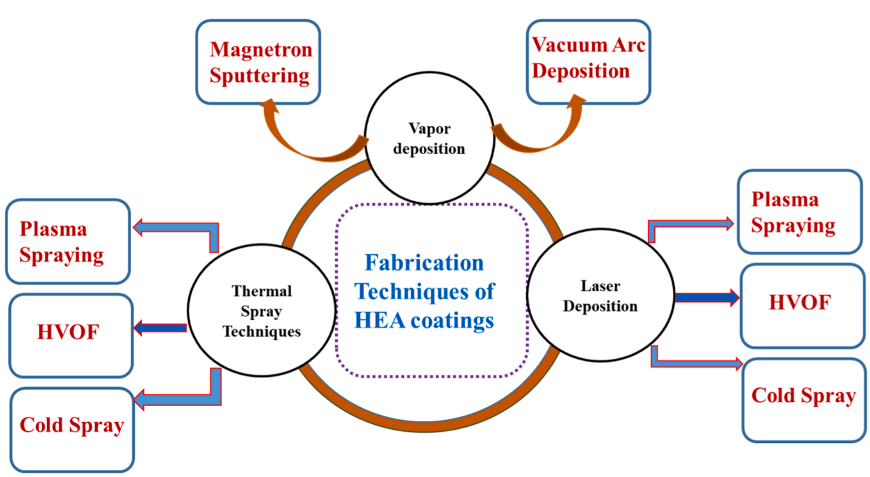

Fig. 14. Fabrication processes of different high entropy alloy (HEA) coatings.

are greatly impacted by the alloy composition and particular manufacturing processes used [186]. Stable single-phase microstructures can be easily formed thanks to the significant mixing entropy present in HEAs. Factors including the quantity of constituent elements, their atomic ratios, and structural features affect how stable certain phases are. HEAs typically have hexagonal close-packed (HCP) crystal structures and single-phase microstructures with face-centered cubic (FCC), body-centered cubic (BCC), or a combination of both [187]. By maximizing elements such the creation of crystal structures, the existence of several phases, and processing techniques, HEAs' mechanical properties can be changed. To examine the effect of crystal structure phase on mechanical properties, Zhang et al. [188]examined CoCrFeNiTiAl HEAs with different Al molar ratios. According to what they discovered, the addition of Al caused the crystal structure to change from FCC to BCC, which improved the compressive strength and elastic modulus. Furthermore, robust nitride bond formation was ascribed to the increased hardness (H) and elastic modulus (E) of (TiVTaNbZrHf)xN coatings, as proven by nanoindentation testing, which yielded values of 13.24 ± 0.21 GPa and 134.33 ± 2.24 GPa, respectively.

The microstructures, mechanical characteristics, corrosion resistance, and wear behavior of high-entropy alloy (HEAs) TixZrNbTaMo (x = 0.5, 1, 1.5, and 2 molar ratios) were investigated. The Vickers microhardness increased from 450 HV to 500 HV, and the yield strength increases from 1440 MPa to 1580 MPa when the Ti concentration in the TiZrNbTaMo HEAs decreased. In particular, the Ti0.5ZrNbTaMo alloy, which has a coarsened dendritic structure, has a notable plastic deformation strain of around 30% and a high compressive strength of 2600 MPa [189]. Gashti et al. [190], using nano-indentation experiments and an applied force of 3 mN, the hardness and Young's modulus of Ti6Al4V and HEA films (TiTaMoVZr) were investigated. The oxide film and the non-oxide HEA layer had depths of 82 nm and 110 nm, respectively, while Ti6Al4V showed an indentation depth of 170 nm. Ti6Al4V has a hardness of 144.8 ± 6 GPa and a Young's modulus of 4.98 ± 0.8 GPa. In comparison, the oxide film revealed 292.5 ± 13 GPa and 30.89 ± 5 GPa for Young's modulus and hardness, respectively, while the non-oxide HEA film gave values of 16.26 ± 2 GPa and 209.1 ± 19 GPa. According to this analysis, the oxide film is around six times tougher than the Ti6Al4V substrate, while the non-oxide film is roughly 3.5 times harder.

Tüten et al. [191] used radio frequency (RF) magnetron sputtering with equimolar TiTaHfNbZr targets on NiTi substrates, expanding on a prior study. This research focused on wear and corrosion resistances, in contrast to its predecessor. Then, using RF magnetron sputtering, an equimolar TiTaHfNbZr high-entropy alloy thin film was formed onto a Ti6Al4V substrate. The coating was particularly noteworthy for its remarkable properties, including its high hardness of 12.51 ± 0.34 GPa and elastic modulus of 181.3 ± 2.4 GPa. Moreover, it showed a lower coefficient of friction and improved wear resistance.

Braic et al. [192] investigation of high-entropy alloy coatings as biomaterials and concentrated on TiZrNbHfTa-based coatings, namely (TiZrNbHfTa)N and (TiZrNbHfTa)C. These coatings were found to be made up of straightforward FCC solid solutions that were orientated in the (111) plane, according to analysis. Examined in simulated body fluid (SBF), the carbide coating demonstrated remarkable wear resistance (μ = 0.12), excellent hardness (~31 GPa), and a non-metal to metal ratio of approximately 1.3. Biocompatibility studies showed that osteoblast cells adhered firmly to the coating, that there were no cytotoxic reactions seen, and that all groups had a high proportion of living cells. As shown in Table 5, several methods can be used to evaluate the mechanical and tribological characteristics of different HEAs, such as hardness, coefficient of friction, and wear rate.

3.3.2. Tribological studies of HEA coated Ti6Al4V alloy

Recently, there has been interest in HEAs, a unique class of multi-component materials, as possible metallic biomaterials for a range of biological applications. They have near-equiatomic proportions of five or more elements in their design, which offers promising properties like high strength and hardness, outstanding corrosion resistance, amazing wear resistance, and structural stability [193]. Metallic implant materials must have certain critical features, such as good biocompatibility, strong corrosion resistance, sufficient mechanical qualities, and high wear resistance, in order to provide a dependable and secure long-term service. The fretting wear rate of TiTaNbMoZr HEA in the presence of biofluids was compared to a control in a study by Kumar et al. [194]. The PS biofluid demonstrated the highest particular fretting wear rate, measuring 1.20×10^{-5} mm^3/Nm, which was around 25% higher than the 5.31×10^{-5} mm^3/Nm specific fretting wear rate seen in the control [194].

Table 5
Previous studies have investigated the properties of nanostructured HEA coatings on AM and commercially available Ti6Al4V substrates.

HEA coatings	Coating Techniques	Mechanical wetting Properties	Wear and Corrosion Properties	Biocompatible coatings	Ref.
TiZrNbHfTa)N and (TiZrNbHfTa)C	Magnetron sputtering	(22.4–32.1) GPa	COF=0.12–0.32, Wear rate= $(0.20–0.90)\times10^{-7}$ mm^3/N.m, E_{corr} (-108.2–52.4) mV I_{corr} (0.287–0.125) μA/cm^2	Biocompatible properties	[192]
TiTaHfNbZr	RF magnetron sputtering	12.51 GPa	COF=0.1–0.2, Wear volume =(3.96–5.75) $\times10^{-2}$ mm^3	Hip or knee joints	[191]
TiZrHfNbTa	-	287–293 HV	E_{corr}(-0.302–0.432) V I_{corr} $(0.8–1.22)\times10^{-3}$A/cm^2	Vitro biocompatibility	[209]
NbTaTiVZr	Magnetron sputtering	5.9–6.5 GPa	E_{corr} (-326–250) mV $I_{corr}$$(27-53)\times10^{-3}$μA/$cm^2$	Orthopedic implants	[214]
TiZrHfNbFe	Magnetron sputtering	770HV	COF= (0.66–0.75), Wear rate=$4.29)\times10^{7}$ mm^3/N.mm, E_{corr} (-0.27) V I_{corr} $(1.66)\times10^{-7}$A/cm^2	Biomedical-implantation	[215]
TiZrNbTaMo	-	Ti6Al4V-320HV – Coated-500HV	Wear rate= $(2.20–2.91)\times10^{-7}$ mm^3/N.mm,	Biomedical implant	[189]
Ti1.5ZrTa0.5Nb0.5W0.5-Ag	RF magnetron sputtering	4.9–18 GPa	E_{corr} (-190.09) mV I_{corr} (0.071) μA/cm^2	Biocorrosion applications	[82]
TiTaMoVZr	Magnetron sputtering	44–46.39° 16.26–30.89 GPa	-	Implant and bone applications	[190]
FeCoNiTiAl	Magnetron sputtering	-	COF=0.32, Wear volume =(0.7–1.2) $\times10^{-6}$ μm^3	Artificial joint	[199]
AlCoCrCuFeNi	Laser alloying setup	1038 HV	COF=0.29–0.31	Bio lubrication property	[200]
$Fe_{22}Co_{22}Ni_{22}Ti_{22}Al_{12}$	Magnetron sputtering	8.5–14.5 GPa	-	Biomimetic artificial bone	[216]

Zhao et al. [195] produced the high-entropy alloys (HEAs) coatings AlNbTaZrx on Ti6Al4V through laser cladding with success. The microhardness of the coatings improved by approximately 17% from $x = 0.2$ to $x = 1.0$ as a result of the increase in x, which facilitated the change from β into α. Compared to the substrate (1.04 mm3, 2.41×10^{-4} mm^3 N^{-1} m^{-1}), the average wear volume and wear rate (0.72 mm^3, 1.66×10^{-4} mm^3 N^{-1} m^{-1}) of the coatings were both reduced by almost 31%. Mu et al. [196] coated TiZrNb films consist of hexagonal α-phase and cubic β-phase columnar crystals. The film deposited at 120 W showed the lowest weight loss and wear rate, measuring 1.2 mg and 7.5×10^{-4} mm^3/Nm, respectively. These values were lower than those of the uncoated substrate by 65.7% and 34.2%, respectively. Wear studies conducted by Zhang et al. [197] reveal that the HEA (FeCuNiTiAl) coating has a wear rate of 0.89×10^{-5} mm^3/(N·m), whereas Ti6Al4V has a wear rate of 53.97×10^{-5} mm^3/(Nm). The HEA coating also increases the wear resistance of the substrate by a factor of 60 [197].

As mentioned earlier, one noteworthy characteristic of HEAs is their great hardness, which significantly reduces wear rates. TiTaHfNbZr HEA coatings, which have high homogeneity, density, and mechanical compatibility with Ti6Al4V substrates, were studied by Tuten et al. [191]. These coatings provide strong resistance to deterioration and cracking, which makes them appropriate for orthopaedic implants used in knee or hip joints that are subjected to dynamic contact loading over an extended period of time [198] [191]. In a different study, TixZrNbTaMo (x = 0.5, 1, 1.5, and 2 molar ratio) HEAs outperformed Ti6Al4V alloy in terms of resistance to both dry and wet wear. The wear resistance of the HEAs increased in tandem with decreasing Ti concentration. The wear rates of TiZrNbTaMo HEA under wet friction conditions were lower than those under dry friction conditions. Among the four HEAs, the Ti0.5ZrNbTaMo alloy exhibited the best resistance to corrosive wear, which improved its biocompatibility and made it a viable material for use in biomedical implants. Consequently, Ti6Al4V wear resistance might be significantly increased by using HEAs as efficient wear-resistant coating materials [189].

3.3.3. *Corrosion resistance of HEA coated Ti6Al4V alloy*

The corrosion resistance of HEAs is another important characteristic that should be considered. The structure of HEAs, which is typified by a disorganised arrangement of many elements, produces a chemical environment that is spatially disordered and increases corrosion resistance. This characteristic has been the focus of several studies over the past ten years and is essential for the application of HEAs as coating materials [189] [82]. Recent research has demonstrated the practical application of HEAs films via laser cladding, magnetron sputtering, and electro-spark deposition on a variety of metallic substrates, including steel, titanium alloys, Al alloys, and Si [199,200].

By blocking the flow of oxygen, HEA films provide corrosion protection by creating a thick, non-crystalline passive layer. These passive layers prevent corrodents from penetrating the substrate and effectively block electrochemical processes below the HEA coating [201]. Selecting the right HEA elements is essential to attaining the best corrosion resistance. By encouraging the production of non-uniform passive films, the addition of elements such as Al or Cu can change the microstructure and lead to elemental segregation, which reduces corrosion resistance. On the other hand, pit formation is less likely when passivation elements like Cr are included since they encourage the production of a homogeneous protective oxide film [202]. In addition to selecting the right components, heat treatments and anodic treatments are important ways to enhanced the protection that passive HEA films offer. Through the reduction of elemental segregations and promotion of microstructural homogenization, heat treatment of HEAs can increase corrosion resistance [202].

3.3.4. *Surface wettability properties of HEA coated Ti6Al4V alloy*

A material's surface energy determines its surface wettability, which affects cell adhesion and protein adsorption and is essential for implant biocompatibility. Implant materials' wetting behaviour becomes crucial when they come into contact with physiological fluids during insertion. Although metals are generally hydrophilic, it is important to create noticeably hydrophobic sheets. Numerous studies have emphasized that high-entropy alloys (HEAs) are hydrophobic. Because of their distinct structures, HEAs have higher electron work function values and are more inert, which decreases their electron interaction with water molecules and increases their hydrophobicity [190] [203].

Few studies have looked at HEAs wetting characteristics on substrates other than Ti6Al4V. Wan et al. [204] studied the wetting behavior of AlCoCuNiSiTi HEA films produced by laser cladding on an X70 steel substrate. According to their results, HEA-coated surfaces are more hydrophobic than uncoated surfaces [204]. Similarly, the results of a further investigation demonstrated the strong hydrophobic characteristics of the AlCrMoNbZr HEA coating, which was applied on N36 zirconium alloy substrates using the magnetron co-sputtering method [205]. Additionally, Wang et al. [206] used magnetron sputtering to deposit CCrMnNi high-entropy alloy (HEA) films onto Si (100) substrates of various thicknesses. Their study focused on how the HEA coating affected the ability of the samples to be moist. The findings showed that applying HEA sheets to the Si (100) substrate significantly boosted its surface hydrophobicity, resulting in a contact angle increase of up to 96°. These hydrophobic surface features that HEAs displayed may impart antibacterial and antifouling qualities [206].

3.3.5. *Biocompatibility properties of HEA coated Ti6Al4V alloy*

Preparing materials for biomedical applications requires optimizing their physical and chemical properties to minimize protein adsorption and cellular interactions while increasing biocompatibility. One of the main strategies for maximizing interactions with the biological environment is coating biomaterial surfaces with materials that have the right chemistry. Compared to typical alloys, high-entropy alloys (HEAs) have a distinct surface chemistry and changeable biocompatibility due to their complicated distribution of different chemical components inside their crystalline structure. This capacity to pick particular mixtures of components allows for the development of better mechanical qualities as well as customized biocompatibility, which is important for medical applications [37] [207].

Thus far, a significant portion of the evaluation process for biomedical high-entropy alloys has focused on their phase stability and mechanical characteristics. The in vivo and in vitro properties of these novel engineering alloys are being studied, nevertheless, thanks to certain recent research initiatives. Akmal et al. investigated the in vivo biocompatibility of MoTaNbTiZr system alloys [208]. The optimized alloy, chosen for its advantageous mechanical qualities, did not exhibit any negative effects or muscle damage during implantation in mice that could have been caused by possible toxicity concerns. Importantly, our study indicates that such effects can be considered equally safe for this alloy system as those noted for well-known biomedical materials such as Ti6Al4V alloys or NiTi shape memory alloys. Yang et al. [209] conducted an assessment of the in vitro compatibility of a TiZrHfNbTa high-entropy alloy. The study demonstrated favorable cell adhesion, viability, and proliferation of MC3T3-E1 cells, indicating the potential of this alloy for biomedical applications [209]. Using human gingival fibroblasts, Wang et al. [210] examined the biocompatibility of a TiZrHfNbTa high-entropy alloy [210]. Guo et al. [211] evaluated the effect of covering implant surfaces with (TiZrNb)14SnMo, a refractory high-entropy alloy. Their results showed that HEA coating significantly improved substrate biocompatibility [211].

To sum up, the alloy showed no signs of cytotoxicity when it came into touch with living tissue. Furthermore, more fibroblasts proliferated in the TiZrHfNbTa alloy than in the TiZrHf equivalent, suggesting better biocompatibility. After seven days of culture, the (TiVTaNbZrHf)N coating's cytotoxicity tests showed no negative cellular reactions and outstanding physicochemical characteristics and cell adhesion. These coatings showed excellent toughness and non-cytotoxic properties. The study's overall findings demonstrate the possibility of sputtering nitride protective coatings to enhance the mechanical qualities of Ti6AlV alloy [191].

High-entropy alloys (HEAs) with refractory elements such as W, Nb, Mo, Ta, and V were first created. Next, HEAs with transitional metals including VNbMoTaW, TaNbHfZrTi, HfNbTaTiZr, MoNbTaVW, and HfMoNbTaTiZr were produced. Except for vanadium, most of these elements have biocompatible characteristics. When compared to pure titanium, HEAs such as TiNbTaZrHf, TiNbTaZrFe, TiNbTaZrMo, TiNbTaZrCr, and TiNbTaZrW exhibit higher biocompatibility, according to a number of studies [83,212]. HEAs are promising for use in biomedicine because of their remarkable mechanical properties, corrosion resistance, and biocompatibility. The use of DLC-coated Ti6Al4V materials is outlined in Table 5, which also includes information on the substrate and coating combination, deposition method, coating characteristics, biocompatibility, and other main advantages.

3.3.6. *The effect of HEA coating thickness on the properties*

Researcher Wang et al. [206] investigated CoCrFeMnNi high entropy alloy films (HEAFs) produced via magnetron sputtering, varying in thickness from 250 to 1400 nm. They explored the relationship between film thickness, surface electron activity, wettability, and corrosion resistance. The 550 nm-thick film, characterized by the smallest nano-scale grain size and highest density of grain boundaries, demonstrated superior properties: it exhibited the highest electron work function (EWF) at 4.2 eV, the most significant hydrophobicity with a water contact angle of 96°, and exceptional corrosion resistance with E_{corr} at −301 mV and I_{corr} at 0.481 μA/cm^2. Gashti et al. [190] investigated TiTaMoZrV film deposition on Ti6Al4V alloys via PVD under air and argon atmospheres. They achieved a uniform, crack-free oxide film by enhancing its surface morphology. Compared to non-oxide films, the oxide variant displayed increased thickness (813–904 nm) and roughness (2.2–4.2 nm). The oxide film exhibited a decreased corrosion rate due to a protective oxide layer, alongside a higher wetting angle (69.86, 46.39, and 44°) enhancing cell adhesion. The films showed increased hardness (16.26 ± 2 GPa to 30.89 ± 5 GPa) with oxide variants having the highest, crack-free hardness. However, the films also displayed an increased elastic modulus compared to Ti6Al4V alloy, potentially leading to stress shielding between implants and bone.

Another study measures film thickness at different deposition times, revealing a gradual increase from 279 nm at 10 minutes to 1.9 μm at 85 minutes, as illustrated in Fig. 16. The resulting alloy coating demonstrates outstanding properties, boasting a remarkably high hardness of 29.2 GPa (±1.5) and an elastic modulus of 321 GPa (±8.9), alongside a smooth surface texture. Notably, it exhibits superior cell viability compared to CP-Ti, with the TiMoVWCr HEA showing enhanced cell viability in MTT assay analysis [213]. Nano-indentation tests on proposed bone materials with various pore diameters of porous scaffolds confirmed that a combination of HEA coating with a thickness of 1.9 μm and porous scaffold with a pore-forming agent diameter of 2.5 μm yielded optimal surface mechanical properties. Elastic modulus and nanohardness of coatings displayed a non-linear relationship with thickness, with coatings deposited for 1 and 2 hours exhibiting higher values compared to those deposited for 0.5 and 3 hours. This disparity is attributed to thinner coatings with shorter deposition times and improved quality with longer times. Notably, coatings deposited for 1 hour exhibited superior quality and mechanical properties, indicating the importance of optimizing coating thickness for enhanced performance.

As indicated in Table S3, the influence of coating thickness on a range of properties emerges as a crucial aspect in the realm of materials science and engineering. The comprehensive data presented underscores the importance of carefully tailoring coating thickness to attain optimal performance across various parameters. Specifically, studies on High Entropy Alloys (HEA) emphasize the necessity of adjusting coating thickness to enhance mechanical strength, corrosion resistance, and biocompatibility.

The mechanical and corrosion/wear resistance of HEAs are improved by the random arrangement of numerous parts. Utilizing HEAs as coatings lowers overall expenses and consumption. Biomedical HEA coatings provide a wide range of surface topographies and exceptional biocompatibility. Equimolar HEA coatings, which have balanced constituent elements and attractive mechanical properties along with enhanced resistance to wear and corrosion, offer a novel approach to alloy design for bioimplants. For orthopaedic or dental implants, the mechanical biocompatibility of the TiZrNbTaFe alloy is promising. Furthermore, because of their unique properties, titanium and its alloys, noble metal, and cobalt-based alloys are frequently used in medical

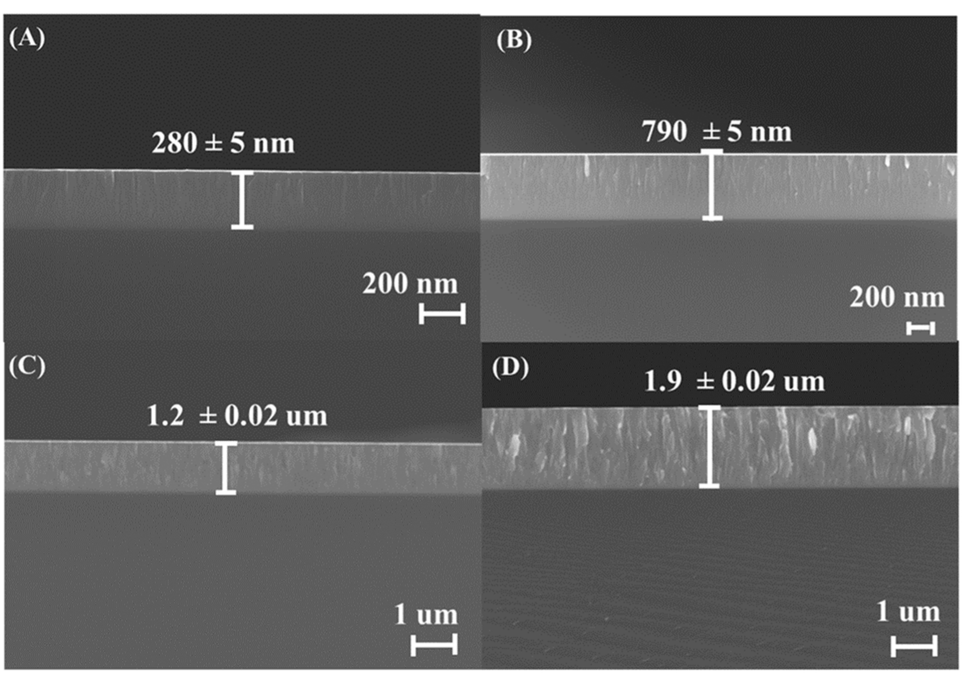

Fig. 16. FE-SEM analysis at different deposition time a) 10 minutes b) 30 minutes c) 60 minutes and d) 85 minutes [213].

applications.

3.4. Metal oxide (MO) and Polymer-metal oxide (P-MO) (composite) biocompatible coatings

Metal oxide nanoparticles possess a distinctive structure, along with intriguing redox and catalytic properties, a large surface area, excellent mechanical stability, and biocompatibility. These characteristics have sparked significant interest in their applications within bio-sensing, bio-imaging, and biomedical therapeutics [217]. These compounds are essential for neurochemical monitoring, cancer diagnosis and therapy, and medical implants. For example, titania's high biocompatibility allows for ideal cell adhesion and growth on its surface, which is why it is often used in medical implants [218]. For their potential uses in biomedicine, gold, iron oxide, aluminium oxide, zirconium oxide, titanium oxide, and zinc oxides have all been well studied. The primary mechanical, corrosion, wetting, and biological characteristics of metal oxide coatings on Ti6Al4V alloys are covered in this section. Metal oxides are inexpensive, stable, and biocompatible, and have multiple uses in biomedical engineering. These uses include drug delivery, therapeutics, bio-imaging, biosensing, functional implants, hearing aids, eye devices, and many other biomedical fields [219].

Moreover, a wide range of biomedical applications make substantial use of polymer and metal oxide coatings. These coatings improve the biocompatibility of many substrates utilised in biomedical contexts, decrease wear, offer antimicrobial characteristics, and increase corrosion resistance. Dip coating, electrodeposition, spin coating (including electro-spinning), and spray coating (including electrospray and ultrasonic spray) are common techniques used for polymer coating deposition [220]. Among other methods, in-situ mineralization and a combination of 3-D printing were used to create ceramic oxide coatings [221]. In this section, we present polymer composite coatings comprising ceramic, carbon, metal and metal oxide as well as silica components aimed at improving biocompatibility in various applications. Metals continue to be more common in orthopaedic applications than biomaterials like polymers and ceramics because of their exceptional physical properties, which include high strength, ductility, hardness, corrosion resistance, formability, and biocompatibility. These characteristics are critical for fulfilling the demanding demands of load-bearing and wear resistance in total joint arthroplasty (TJA) and fracture fixing [222]. Orthopaedic biomaterials are typically classified into subcategories related to pediatrics, trauma, and reconstruction within the lower or upper spine extremities [223].

3.4.1. Composite coatings of MO and P-MO composite coated Ti6Al4V alloy

Metals are a broad category of inorganic materials with special qualities such as electronic conductivity, magnetic characteristics, catalytic activity, particle surface plasmon resonances, and antibacterial properties. Fig. 17 presents a wide range of sophisticated metal oxide and nanopolymer composite coatings and highlights their critical function in surface modification of Ti6Al4V orthopaedic bio implants. In the difficult biomechanical environment of the human body, these coatings offer a novel way to improve the functionality and lifetime of orthopaedic implants. These metal oxides and nanopolymer composite coatings play a major role in the success and dependability of orthopaedic implant treatments by efficiently altering the surface characteristics of Ti6Al4V implants, such as enhancing biocompatibility and decreasing wear. They are widely used in the field of orthopaedic biomaterials, as seen by their substantial representation in Fig. 17. Examples of metals are silver (Ag), copper (Cu) iron (Fe), and gold (Au). These characteristics render metals adaptable to a wide range of uses, particularly in the biological domain. Furthermore, the use of magnesium (Mg) in orthopaedic applications has attracted a lot of attention in recent

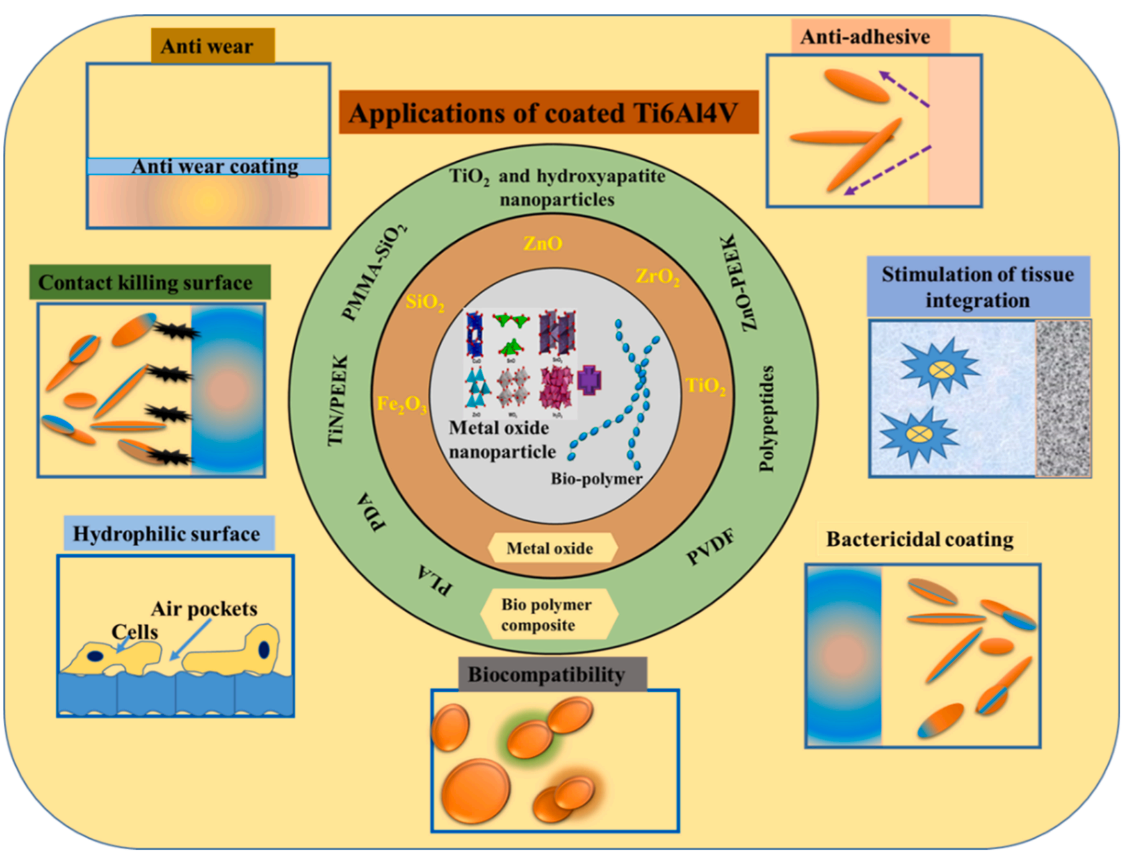

Fig. 17. Different advanced metal oxide (inorganic) and Polymer -metal oxide (composite) coatings employed for modifying the surface of Ti6Al4V orthopedic bio implants and their applications in various biomedical settings.

years. It exhibits promising potential in biological situations since it improves osteoconductivity and degrades non-toxically [39]. PU/Mg coatings were created by Abdal-hay et al. [193] by creating a combination solution of Mg powder and PU pellets, which was subsequently spin-coated onto Ti substrates. These composite coatings demonstrated increased osteoblastic-like cellular adhesion and proliferation in addition to better corrosion resistance [224].

Metal oxide nanoparticles, including TiO_2, ZnO, ZrO_2, and Fe_3O_4, display distinctive characteristics such as adsorption behavior, ligand sequestration, thermal stability, magnetic activity, biocompatibility, optoelectronic properties, and antibacterial ability. Consequently, metal oxides find wide applications in separation processes, solar cells, functionalization of implants, catalysis, biosensing, bioimaging, and drug release systems [39]. Clay minerals, cement, glass, and other materials are examples of ceramics, which are made up of both metallic and non-metallic elements such as oxides, phosphates, or carbides. Calcium phosphate, calcium sulphate, carbonate, and bioactive glasses are examples of common varieties. These materials have great potential for use in biomedical fields, especially in tissue engineering, where the main goal is to regenerate bone tissue [225].

3.4.2. Mechanical properties of MO and P-MO composite coated Ti6Al4V alloy

Improving the mechanical qualities of the final product is the main justification for adding inorganic particles to polymer matrices. This comprises, as described in theories of nanocomposite materials, enhancements in tensile strength, hardness, Young's modulus, flexural strength or stiffness through reinforcement mechanisms [226]. In a study by [194], three different coatings were applied by plasma spraying onto Ti6Al4V (TAV) alloy: (i) AO, (ii) 8 mol% yttria stabilised zirconia (8YSZ), and (iii) Alumina-40 wt% 8YSZ composite (A4Z). Higher than the 8YSZ and A4Z composite coatings by 1.65 and 1.2 times, respectively, the alumina coating had a harder surface (9.43 ± 3.5 GPa). The mechanical characteristics of polymer composite samples made of calcium carbonate and ABS (acrylonitrile butadiene styrene) were also examined in this study [227] [228].

ABS/micron-sized particle composites showed a greater Young's modulus but lower tensile and impact strengths compared to pure ABS, while ABS/nanoparticle composites showed increased impact strength and Young's modulus. Al_2O_3 nanoparticles were added to polyester resin systems that were theoretically brittle to increase their fracture toughness. Wang et al. [229] examined the Al_2O_3/polymer nanocomposite coatings tribological and electrochemical corrosion behaviours in their investigation. They used electrochemical methods, such as potentiodynamic polarisation measurements, micro-hardness testing, single-pass scratch testing, and abrasive wear testing. The polymer coating to scratches and abrasions was improved by the addition of Al_2O_3 nanoparticles.

Singh et al. [230] used a Ti6Al4V alloy and a plasma deposition procedure to create biomimetic nanoporous 50HA-50TiO_2 composite surface for orthopaedic applications. The composite coating tests showed that the HA/TiO_2 coating on the Ti6Al4V substrate surface had hardness and roughness values of 277 HV and 3.59 µm, respectively. The Ti6Al4V alloy surface was successfully modified by HA–TiO_2 coating to satisfy the requirements of orthopaedic implants. Moreover, Song et al. [84], ZrO_2 nanoparticles were introduced to a PEEK matrix at different weight percentages (2, 5, 10, and 15 wt%) in Song et al. study [198]. The coatings' micro-hardness was significantly enhanced by the inclusion of nanoparticles; the sample containing 5 wt percent ZrO_2 (Z1) had the highest value, 356.8 HV0.1. Other coated samples displayed micro-hardness values that were substantially lower than Z1, with Z2 measuring only 16.9 HV, or 4.7% of Z1. Furthermore, as the weight percentage of ZrO_2 nanoparticles in PEEK coatings increased, the micro-hardness values increased as well, reaching 18.0, 20.8, and 26.3 HV for coatings containing 10 wt%, 15 wt%, and 5 wt% of ZrO_2 nanoparticles, respectively. According to the study's findings, the PEEK covering with five weight percent ZrO_2 nanoparticles had the best tribological properties for use as a bearing.

3.4.3. Tribological properties of composite coated Ti6Al4V alloy

A major issue with total joint arthroplasty failure is plastic component wear, which is usually caused by ultra-high molecular weight polyethylene (UHMWPE) composition. Therefore, one of the main challenges facing orthopaedic research is minimizing joint wear. Surface coatings and treatments are recognized as cutting-edge methods for improving tribological characteristics, especially in orthopaedics. Positive tribological capabilities were observed by Berni et al. [201] when they examined yttria-stabilized zirconia (YSZ) coatings applied on titanium components sliding against UHMWPE inserts. When dry and lubricated, the wear rates of the coated samples were around 17% and 4%, respectively, less than those of the uncoated samples. Moreover, the tribological performance of graphene oxide (GO) coatings may be improved by the existence of a DA transition layer, according to experimental findings [85] [231].

Researchers [232] investigators observed that the friction coefficient of untreated Ti6Al4V varied between 0.28 and 0.64 over time. However, during a 300-second friction experiment, the friction coefficient of M-TamOn coating ranged from 0.1 to 0.15, showing less variability compared to the TamOn film (0.19–0.3). Moreover, the average friction coefficient of M-TamOn coating was 0.13, representing a 50% reduction compared to the TamOn coating. Many studies have explored hydroxyapatite (HA) coatings to enhance bone implants due to HA's high bioactivity, biocompatibility, and low elastic modulus. The coefficients of friction (COF) and wear rates in dry friction and simulated body fluid (SBF) lubrication in the study by Tain et al. [202] were as follows: Ti6Al4V > Ti-HA > Ti-Fe_3O_4/HA. These results imply that the tribological performance of the titanium alloy was greatly enhanced by the Fe_3O_4/HA coating. The main factor that led to the improvement in tribological properties was the change in friction mechanisms on the Ti-Fe_3O_4/HA surface from sliding friction to rolling friction behaviors [233].

Moreover, the crystallinity of the PEEK 708 polymer influences the tribological properties of Si_3N_4/PEEK 708 coatings. With a specific wear rate of 1.41×10^{-6} mm^3/Nm and a coefficient of friction (COF) of 0.26, the semi-crystalline coating exhibits exceptional performance. On the other hand, amorphous coatings show greater COF (0.31) and wear rates (4.74×10^{-6} mm^3/Nm). With a wear rate of 2.61×10^{-6} mm^3/Nm, the semi-crystalline Si_3N_4/PEEK 708 coating significantly outperforms the polymer coating in terms of wear resistance [234]. Researcher [235] explored the tribological properties of a graphene oxide (GO)-poly(vinyl pyrrolidone) (PVP) (PGO) coating on micro-textured Ti6Al4V alloy surfaces. The PGO coating notably improved the frictional behavior, reducing the friction coefficient by 1.4 times compared to the as-received alloy. Furthermore, the friction coefficient was significantly reduced to less than 0.03 by applying a dual-layer GO-PVP coating. The coefficient of friction was significantly reduced when coatings consisting of a polyetheretherketone-based TiN/PEEK708 nanocomposite were applied to substrates made of titanium alloy that had been oxygen-hardened. The base alloy's coefficient of friction was reduced to 0.30 by these coatings, from 0.70 for the oxygen-hardened alloy and 0.65 for the base alloy. Moreover, they markedly improved the alloy's wear resistance in dry sliding contact with an alumina ball. When compared to the untreated oxygen-hardened alloy and the base alloy, the covered oxygen-hardened alloy's wear rate was reduced by a factor of 70 and 650, respectively [235].

Using metal oxide coatings to reinforce the materials, the study examined the tribological characteristics of metal oxide and polymer composites. Tables 6 and 7 provide a succinct summary of the conclusions and pertinent data. These tables most likely offer information on the composites tribological properties under many circumstances and compositions, including hardness, wear rate, coefficient of friction, and others.

Table 6
The characteristics of nanostructured metal oxide coatings on commercially available Ti6Al4V substrate and AM have been studied in the past for biomedical applications.

Metal oxide coatings	Coating Techniques	Mechanical and wetting Properties	Wear and Corrosion Properties	Biocompatible coatings	Ref.
ZnO, ZnO-Ta_xO_y	Magnetron sputtering	98.71–101.47°	Icorr- (3.85–1.12) μA/cm^2	Orthopedic Application	[221]
ZnO–ZrO_2 nanoparticles into TiO_2	Plasma electrolytic oxidation process	12.5–55.5°	Ecorr =(0.121–0.314) mV Icorr- (10.45–2.37)× 10^{-8}A/cm^2	Antibacterial effects	[253]
ZnO	Two-step nanosecond laser treatment	61.3–62.1 °	-	Biomedical implants	[260]
SiO_2 and SiO_2-ZnO	Electrophoretic deposition	-	Ecorr =(-165.01–3.67) mV Icorr- (0.271–0.051) mA/cm^2	Biomedical applications	[261]
Zn-ZrO_2/TiO_2	Magnetron sputtering and micro-arc oxidation (MAO)	-	Ecorr =(0.031–0.113) V Icorr- (6.809–5.66) A/cm^2	Antimicrobial property, cytocompatibility	[254]
ZnO	Two-step laser processing	63.8–75.2 °	-	Osteogenic and antibacterial ability	[262]
ZrO_2	Plasma electrolyte oxidation (PEO)	65–80 °	E_{corr} =(389−576) V I_{corr}- (42.60–18.50) A/cm^2	Antibacterial effect	[255]
TiO_2 and ZrO_2	Plasma spray deposited	25–55 °	E_{corr} =(-1.12–0.98) V I_{corr}- (1.26×10^{-5} −9.88×10^{-6}) A	Biomedical applications	[263]
TiO_2/ZrO_2	Plasma electrolytic oxidation process	71–90 °	E_{corr} =(450−611) mV I_{corr}- (18.50–53.92) nA/cm^2	Biomedical applications	[255]
TiO_2, ZrO_2, and TiO_2/ZrO_2	Atomic layer deposition	-	E_{corr} =(-0.11–0.69) V I_{corr}- (5.8–7.2) ×10^{-8} A/cm^2	Dental implants	[264]
ZrO_2	Pulsed Plasma Deposition	11.1 GPa	COF=0.13, Wear rate=1.06×10^{-5} mm^3/N.m	Orthopedic applications	[85]
ZrO_2, PEEK/ZrO_2	Dip-coating	16.9–26.3 HV	COF=0.237–0.120	Cervical discs	[84]
TiO_2	Electrolytically coating	-	E_{corr} =(-191) V I_{corr}- (0.03) μA	Biocompatibility, and cell integration	[265]
TiO_2	Laser cladding	55.6–71.3°	-	Bioactivity and cyto-compatibility	[241]

Table 7
Previous studies have investigated the properties of nanostructured inorganic-polymer composite coatings applied to additive manufacturing (AM) substrates and commercially available Ti6Al4V materials.

Inorganic-polymer coatings	Coating Techniques	Mechanical and wetting Properties	Wear and Corrosion Properties	Biocompatible coatings	Ref.
Poly-ε-caprolactone-TiO_2	Dip-coating technology	-	-	Bioactivity improvement	[259]
Mg-doped chitosan-gelatin	Electrophoretic deposition (EPD)	-	-	Vitro cellular, pre-osteoblast cells	[266]
Chitosan, TiO_2 nanoparticles (TO) and hydroxyapatite nanoparticles	Dip-coating technology	-	E_{corr}-(-304–120) mV I_{corr}- (2.5–0.41) μA/cm^2	Orthopaedic implant	[220]
ZrO_2/PCL composites	Sol-gel dip-coating	-	-	Osteointegration implanted in vivo	[248]
Selenium-Doped Hydroxyapatite	Sol- gel dip-coating	-	-	Orthopedic implants	[267]
Fumed Silica/Chitosan/Poly (vinylpyrrolidone)	Dip-coating technology	-	E_{corr}-(-380–306) mV I_{corr}- (39.8–0.1) A/cm^2	Artificial Saliva Solution	[119]
PEDOT: PSS@TiO_2 layer	Spin-coating	2.84–31.80°	E_{corr}-(-233–92) mV I_{corr}- (2.01–1.30)×10^{-7}A/cm^2	Biocompatibility	[268]
HA-TiO_2 composite	Plasma deposition process	977 HV	-	Orthopedic Applications	[230]
PMMA-SiO_2	Dip-coating	-	-	Biomaterial applications	[269]
Ceramic-polymer	Wet chemical synthesis	-	-	Orthopaedics	[40]
poly(D, L-lactide)	Spin-coating	-	COF=0.36	Endosseous implants	[270]
Chitosan-Bioactive glass (CS-BG)	Cathodic electrophoretic deposition (EPD)	74.71–64.65°	E_{corr}-(-0.28–0.22) mV I_{corr}- (7−2) ×10^{-7}A/cm^2	Orthopedic applications	[271]
Diazonium salt-polyurethane	Dip-coating	-	COF=0.054–0.23	Orthopedic industry	[272]
TiN/PEEK708	Cathodic electrophoretic deposition	-	COF-0.65–0.30, Wear rate = (79–1.1) ×10^{-6} mm^3/N.m	Biomaterial applications	[273]

3.4.4. *Corrosion resistance of MO and P-MO composite coated Ti6Al4V alloy*

Orthopaedic and dental implants' difficulties with Ti6Al4V alloy have led to the development of poly (methyl methacrylate)-silicon dioxide (PMMA-silica) coatings as a potential remedy. These coatings are used to act as a bioactive film and an anticorrosive barrier on the surfaces of Ti6Al4V alloys. Strong adhesion, low porosity, mechanical resistance, heat stability, and superior barrier qualities are some of their key characteristics that contribute to their efficiency. PMMA-silica hybrid coated steel, in particular, showed remarkable performance, displaying impedance values as high as 10 GΩ cm^2, which held steady in a typical 3.5% NaCl solution for more than six months [236]. Wei and colleagues have demonstrated that the PMMA-silica system exhibits significant advantages as dental restorative materials when compared to dental amalgams, porcelains, and silicate cements. These advantages include improved esthetics, enhanced corrosion properties, thermal conductivity, tensile strength elimination of galvanic currents, solubility and toughness [237].

Manam et al. [238] examined an implant material's bio-corrosion behavior, realizing that this behavior plays a critical role in defining the material's functionality and biocompatibility. Bio-corrosion tests were performed for all nanocomposite coatings (CS-BG) and the uncoated Ti6Al4V specimen using polarization and electrochemical impedance spectroscopy (EIS) examinations in simulated bodily fluid (SBF) solution at 37°C after 1-hour immersion in open circuit potential (OCP). The sample with the highest E_{corr} value, CS-1.5 g/L BG coating, showed noticeably better corrosion resistance for Ti6Al4V than the other samples. These results imply that orthopaedic applications could benefit greatly from nanocomposite coating samples with good corrosion resistance, appropriate bioactivity, and sufficient cell survival.

3.4.5. Wetting properties of MO and P-MO composite coated Ti6Al4V alloy

The hydrophilic/hydrophobic surface of Ta, Zr, Ti, and Nb oxide films produced by magnetron sputtering has a major effect on albumin adsorption. Significantly, the maximum albumin adsorption was observed on the hydrophobic surface. The adsorption process was shown to be governed by a number of different physicochemical mechanisms, which varied according to the surface wettability [239]. The amount of albumin adsorbed on hydrophilic surfaces was strongly correlated with the polar component of surface energy. By oxidising Ti discs with H_2O_2, Nagassa et al. [209] produced a hydrophilic surface that promoted high albumin adsorption. The adsorption of albumin generally rises with surface hydrophobicity. In this case, however, the oxidising treatment changed the chemical ending groups on the surface without substantially altering its hydrophilic character, and it also enhanced surface roughness and TiO_2 thickness. Because of the oxidation process's changes, the TiO_2 layer surface showed increased albumin adsorption while maintaining hydrophilicity comparable to the untreated Ti surface [240].

Contact angle measurements were made on room-temperature simulated bodily fluid (SBF) droplets on surfaces such as FGM cladding, 100% HA, and non-cladded Ti6Al4V in the study by researcher [241]. The observed contact angles were 60.6° for FGM cladding surfaces, 71.3°, and 91.9 °for 100% HA, and non-cladded Ti6Al4V, respectively. These results show that using 100% HA and FGM laser cladding procedures increases the hydrophilicity of the non-cladded Ti6Al4V surface. Superhydrophobic TiO_2 coatings were created on biomedical Ti6Al4V alloys by Jiang et al. [242] using the micro-arc oxidation (MAO) process followed by a superhydrophobic treatment. The uncoated Ti6Al4V alloy, the MAO-treated sample, and the MAO-treated sample that underwent superhydrophobic treatment all had their water contact angles tested. After the MAO treatment, the Ti6Al4V alloys water contact angle initially went from 69.70° to 52.11°, but it then sharply increased to 153.39° following the superhydrophobic treatment. The TiO_2 coating's superhydrophobic surfaces on the Ti6Al4V alloy may improve the in vitro hemocompatibility of the alloy, as indicated by the increase in hydrophobicity.

The wetting angle increased as a result of atomic layer deposition (ALD) surface alteration. The contact angle of the ZnO-coated sample was 110°, whereas that of the untreated Ti6Al4V sample was 63°. The hydrophobic nature of the surface is indicated by a contact angle value greater than 90°. Furthermore, when diiodonomethane was utilised as the measurement liquid, comparable contact angle values 45° for the uncoated sample and 54° for the ZnO-coated sample were found for both sample groups [243].

The combination of metal oxide (TiO_2) produced by plasma electrolytic oxidation on Ti substrates and poly-ethylenedioxythiophene-polystyrenesulfunate (PEDOT: PSS) was studied by researcher Kamil et al. [244]. The water contact angle was one of the surface attributes that was greatly affected by surface modification. The naked plasma electrolytic oxidation (PEO) layer had a low contact angle of 2.84° prior to PEDOT: PSS deposition, which was explained by the high surface energy from the plasma exposure during PEO. The contact angle increased to 37.84°, 34.82°, and 31.81° after the addition of the PEDOT: PSS layer, demonstrating its hydrophilicity. The significant change in contact angles highlights the surface property modification caused by the newly developed PEDOT: PSS layer, even though it is hydrophilic.

3.4.6. Biocompatibility of MO and P-MO composite coated Ti6Al4V alloy

Silver (Ag), renowned for its antimicrobial properties, is frequently employed in medical applications. Rana et al. fabricated chitosan-silver-gelatin (CS/Ag/Gel) films incorporating the model drug Metronidazole. The incorporation of silver nanoparticles (Ag NPs) in small quantities notably enhanced cell proliferation and facilitated drug release in vitro, while chitosan (CS) and gelatin (Gel) exhibited excellent biocompatibility [245]. Rather than using gelatin Mishra et al. [246] chose poly (vinyl alcohol) (PVA), a highly compatible biodegradable polymer. Ag-PVA nanocapsules were created and subsequently incorporated into composite systems containing chitosan (CS). Titanium substrates were uniformly coated with the resultant slurry. By selectively entrapping the drug within the Ag-PVA nanocapsules, these composite coatings not only guaranteed biocompatibility but also successfully inhibited biofilm development and permitted prolonged drug release.

Using gold nanoparticles (GNPs), which are well-known for their photothermal properties, biocompatibility, and ease of modification, Yu et al. created a novel antibacterial coating. A phase-transitioned lysozyme film (PTLF) and a GNPL layer were successively deposited as part of the coating process. While the PTLF served as a sacrificial layer in the vitamin C solution to remove dead bacteria and regenerate bactericidal activity, the photothermal characteristics of GNPL enabled effective eradication of bacteria [247]. To treat infected hernias, Zhao et al. modified polyurethane (PU) substrates using polyethylene glycol (PEG) and gold (Au). To increase their reactivity with Au, PU and PEG were subjected to thiol modification. To generate PU-Au samples, a solution of Au nanorods (NRs) was applied to the thiol-modified PU and allowed to dry. These samples were then submerged in a PEG solution. The resultant Au/PEG coatings demonstrated intrinsic antifouling qualities from PEG and photothermal bactericidal properties caused by near-infrared (NIR) radiation from Au, indicating potential for the treatment of illnesses linked to biomedical devices.

Magnesium (Mg) has attracted much attention recently owing to its potential for orthopaedic applications because it can increase osteoconductivity and degrade non-toxically. Abdal-hay et al. created PU/Mg coatings by spin-coating titanium (Ti) substrates with a mixed solution consisting of PU pellets and Mg powder. These composite coatings improved osteoblastic-like cell adhesion and proliferation while demonstrating excellent corrosion resistance [39] [224]. Catauro et al. [248] investigated the modification of titanium discs by depositing layers of TiO_2/poly-ε-caprolactone (PCL) via the sol-gel dip-coating method in the context of biocompatible applications. In order to prepare the inorganic component, PCL had to be incorporated after Titanium (IV) butoxide solution was used. The resulting coatings showed improved resistance to corrosion and wear, as well as bioactivity that might cause hydroxyapatite (Hap) to develop in simulated bodily fluid (SBF). Notably, the creation of coatings free of cracks was aided by the PCL component's inclusion. Fekry et al. [220] created a novel nano-composite film coating on a titanium alloy by electrochemically depositing chitosan (CS), titanium dioxide nanoparticles (TiO_2 NPs), and hydroxyapatite nanoparticles (HAp NPs) on the titanium alloy, which acted as the working electrode. These novel coatings demonstrated enhanced antibacterial and corrosion resistance, which made them useful for orthopaedic applications.

Additionally, researcher Patil et al. [249] fabricated CS/ZnO nanoparticles (NPs) and applied them onto silk fibroin-polyvinyl alcohol (SF/PVA) composite films using a sonochemical approach. This coating method led to enhancements in the swelling degree and mechanical properties of the films. Moreover, the CS/ZnO coatings exhibited cytocompatibility and antibacterial properties, suggesting the potential of the film as a promising wound dressing material. Arias et al. used the electrophoretic deposition (EPD) method on stainless steel electrodes to create composite coatings made of ZnO/bioactive glass/alginate (Alg). Antibacterial characteristics were added by using ZnO nanoparticles, and the production of a hydroxyapatite (HAp) layer was aided by the presence of bioactive glass [250]. Du et al. [251] employed a multistep process to create composite coatings that had high adhesion and antibacterial qualitiesZnO nanorods (ZnO-NRs) were coated on Mg–MgO after MgO coatings were first produced on Mg alloy (Mg/MgO) through the use of micro-arc oxidation (MAO). The resulting coatings, Mg/MgO/ZnO-NRs/(DS/Lys)30, demonstrated good hemocompatibility, robust antibacterial activity, and enhanced corrosion resistance.

3.4.7. The effect of MO and P-MO composite coating thickness on the properties

The impact of coating thickness on properties is significant and varied for both metal oxide and polymer-metal oxide composite coatings. Thicker coatings typically offer improved mechanical strength, wear resistance, and corrosion protection, prolonging substrate lifespan. However, their wetting behavior may differ, affecting liquid adhesion. In biomedical applications, thicker coatings can enhance mechanical stability and tissue integration but require surface modification for optimal biocompatibility. Conversely, thinner coatings prioritize toughness and may promote cell adhesion, beneficial for implants [252]. Achieving an optimal balance is crucial, considering factors like material composition and deposition technique. Overall, coating thickness shapes mechanical, wear, corrosion, wetting, and biomedical properties, necessitating careful optimization in design and application.

Ding et al. [221] investigated the application of a ZnO doped tantalum oxide (TaxOy) multilayer composite coating onto Ti6Al4V titanium alloy through magnetron sputtering. They found the coating thickness to be 3.97 µm for Ta_xO_y and 5.2 µm for ZnO-TaxOy samples. The adhesion strength of the multilayer ZnO-Ta_xO_y coating was significantly higher, approximately 16.37 times that of the single-layer Ta_xO_y coating. Moreover, electrochemical corrosion testing demonstrated superior corrosion inhibition properties of the ZnO-Ta_xO_y composite coating, with higher corrosion resistance and antibacterial properties in biomedical applications. Additionally, the impact of ultra-thin atomic layer deposition (ALD) films, specifically TiO_2, ZrO_2, and mixed TiO_2/ZrO_2 oxides, with a uniform thickness of approximately 30 nm, on the corrosion behavior of Ti6Al4V alloy discs in artificial saliva simulating oral conditions. Despite their thinness, these coatings significantly influence corrosion behavior, evidenced by lower corrosion rates and potentially improving patient satisfaction with dental implants [xx].

Nadimi et al. [253], investigated the influence of incorporating ZrO_2 and ZnO nanoparticles on plasma electrolytic oxidation (PEO) coatings. Notably, the effect of coating thickness on enhancing corrosion resistance, particularly when incorporating specific nanoparticle compositions such as zirconium and zinc oxides, which also contributed to enhanced antibacterial properties due to their compatibility with the human body environment. Moreover, researchers [254] investigated porous Zn-ZrO2/TiO_2 coatings with a thickness of 13 µm, which were fabricated on Ti6Al4V substrates using a hybrid process that combined magnetron sputtering and micro-arc oxidation. The coating consists of two regions: an 11 µm thick porous layer and a 2 µm thick barrier layer adjacent to the substrate. This barrier effectively prevents the dissolution of metal ions into body fluids, inhibiting substrate corrosion. The absence of discontinuity between the oxide film and the substrate signifies strong bonding. These biocompatible coatings exhibit superior corrosion resistance, providing a stable interface for cell attachment and growth, thus enhancing cytocompatibility [254]. However, samples with 3 g/l and 5 g/l ZrO_2 exhibited average thicknesses of around 10.7 µm and 12.7 µm, respectively, attributed to voltage-time curve differences. Higher ZrO_2 concentrations correlated with reduced hydrophilicity, with the lowest contact angle in nanoparticle-free samples. Additionally, antibacterial activity decreased as ZrO_2 concentration increased, highlighting the complex relationship between coating thickness and microstructure, wettability, antibacterial efficacy, and corrosion resistance [255].

Additionally, the thickness of the P-MO composite coatings has a substantial and diverse impact on a number of aspects, such as mechanical, wear, corrosion, wettability, and biological applications. Yigit et al. [256] explored nano-hydroxyapatite (nHA) based coatings reinforced with graphene nanosheets (GNS) on Ti6Al4V alloys via AC-plasma electrolytic oxidation (PEO). They observed increased coating thickness and hardness with higher GNS percentages and deposition frequency, crucial for enhancing implant applications. Novel strategies, like hybrid or composite coatings incorporating Ca- or P-compounds, improve biocompatibility with bone tissues. Coatings with 1.5 wt% GNS at 2000 Hz exhibited surface hardness around 670 HV, significantly higher than uncoated Ti6Al4V. Thicker coatings and reduced pore sizes enhance corrosion resistance and passivity. Maintaining low surface roughness is vital for improved corrosion prevention, as highlighted by Qaid et al. [257] and Ryu and Shrotriya [258]. These findings stress the interplay between coating parameters and properties, underscoring the need for optimized coatings for superior implant performance and longevity.

The coating thickness range of 2.7 µm to 11.3 µm measured by Catauro et al. [259] indicates a significant diversity in the coatings thickness. Additional results from nanoindentation testing under various applied loads showed depths ranging from 440 nm to 630 nm. Remarkably, the thickness of the poly(ε-caprolactone) (PCL) content did not significantly change when the applied load varied, suggesting that the substrate plays a role in deformation mechanisms because of the coatings' restricted thickness. When coated samples were compared to the bare Ti6Al4V alloy, it was seen that there was a notable shift in corrosion potential (E_{corr}). Specifically, PCL-based coatings showed a more dramatic drop of around 400 mV, whereas TiO_2-coated samples saw a shift of about 300 mV. This emphasises how coating thickness affects characteristics like corrosion resistance and raises the possibility that thicker coatings could provide better corrosion protection.

The data provided in Table S4 and S5 of the supplementary material highlights the significance of MO and P-MO coatings thickness on various properties in materials science and engineering. Specifically, the thickness of inorganic-polymer composite coatings plays a critical role in shaping their mechanical, wear, corrosion, wetting, and biomedical properties. Information regarding the utilization of metal oxide and metal oxide-polymer composite coatings on Ti6Al4V substrates, including the deposition technique, coating properties, biocompatibility, and key advantages, is comprehensively outlined in Tables 6 and 7.

Analysis of the data from Table 6 indicates that TiO_2 metal oxide coating is extensively utilized in dental and orthopedic fields owing to its superb biocompatibility and desirable mechanical characteristics. Moreover, TiO_2 is widely used in biomedical applications, especially in bone and tissue engineering, owing to its ability to enhance cell adhesion, osseointegration, and cell migration, and facilitate wound healing.

Analysis of the data from Table 7 suggests that scaffolds made from PLA, PGA, and their copolymers exhibit suboptimal degradation properties. PEEK emerges as a preferred polymer for biomedical applications. Furthermore, there is a growing interest in composite coatings integrating Zirconium dioxide (ZrO_2) and polymers. Similar to the widespread use of TiO_2 and ZnO, ZrO_2, a metal oxide, finds frequent application in the biomedical sector, particularly in implant technology.

According to Tables 6 and 7, metal oxides reinforced with biocompatible polymer coatings offer significant advantages for biomedical applications. The inherent properties of metal oxides, including high surface area, stability, and biocompatibility, are enhanced by the protective biocompatible polymer coating. This combination allows for precise control over surface properties, crucial for promoting cell adhesion, tissue integration, and overall biocompatibility. The polymer coating acts as a biocompatible interface, minimizing the risk of adverse reactions when in contact with biological tissues, making it pivotal for implants, drug delivery systems, and other medical devices. Furthermore, the polymer coating functions as a matrix for controlled drug delivery, facilitating sustained release of therapeutic agents for improved treatment efficacy with minimal side effects. The synergy between metal oxides and polymer coatings results in materials with superior mechanical strength, flexibility, and durability, addressing critical needs in applications such as bone implants and tissue engineering scaffolds. Moreover, the polymer coating acts as a protective layer, preventing metal oxide degradation or corrosion in biological environments, ensuring prolonged material stability for enduring biomedical use.

4. Discussion

Ti6Al4V alloys stand out as highly desirable materials for biomedical applications owing to their biocompatibility, non-toxicity, and exceptional mechanical properties. The advent of additive manufacturing (AM) techniques, including powder bed fusion (PBF) and directed energy deposition (DED), has revolutionized the fabrication of bio-implants, allowing for the creation of intricate designs with remarkable precision. To further enhance the performance of biomedical devices such as implants and catheters, surface modification through various coating methods has become indispensable. Researchers are actively investigating a range of materials for coatings, each offering unique advantages. Transition metal nitrides and metal oxides, notably titanium nitride (TiN), demonstrate excellent wear and corrosion resistance, making them particularly attractive for orthopedic applications. Diamond-like carbon (DLC) coatings, renowned for their superior hardness and low friction coefficients, are ideal for use in orthopedic implants where durability and reduced friction are crucial.

High entropy alloys (HEAs) present intriguing possibilities due to their unique surface chemistry and tunable biocompatibility. Despite their higher cost compared to conventional alloys, efforts are underway to optimize their use as coating materials to enhance corrosion resistance, wear resistance, and biocompatibility in biomedical applications. Metal oxide nanoparticles have also garnered attention for their distinctive properties in biomedical therapeutics and biosensing applications, showing potential for advanced biomedical coatings. Inorganic-polymer composite coatings offer a promising avenue for overcoming the limitations of individual materials. By combining the flexibility and biocompatibility of polymers with the mechanical strength of inorganic materials, composite coatings can provide enhanced performance. For instance, composites incorporating chitosan and titanium dioxide (TiO_2) mimic the composition of bone tissue, offering improved biocompatibility and corrosion resistance for orthopedic implants.

Moreover, the impact of coating thickness on properties like mechanical strength, wear resistance, corrosion resistance, wetting behavior, and biocompatibility is significant across various coating types including metal nitride, DLC, HEA, metal oxide, and polymer-metal oxide. Thicker coatings generally offer better mechanical and wear resistance, along with improved corrosion protection, prolonging substrate lifespan. However, thicker coatings may exhibit different wetting behavior, impacting liquid adhesion. In biomedical applications, thicker coatings can provide enhanced mechanical stability and tissue support, but surface modification is vital for biocompatibility. Conversely, thinner coatings may prioritize toughness and cell adhesion, particularly beneficial for biomedical implants. Balancing these factors is crucial for optimizing coating thickness based on material composition, deposition method, and desired properties. Overall, coating thickness significantly influences the mechanical, corrosion, wear, wetting, and biocompatibility properties of coatings, necessitating careful consideration and optimization in their design and application.

To summarizing key ASTM and ISO standards commonly utilized for assessing coating properties and thickness in below Table 8. This table provides a brief overview of some commonly used ASTM and ISO standards for evaluating coating properties such as adhesion, hardness, corrosion resistance, wear, wetting, biocompatibility and thickness.

Overall, the exploration of various coating materials and techniques underscores the ongoing quest to optimize the performance and biocompatibility of biomedical devices. Through interdisciplinary research and innovative approaches, scientists are advancing the field of biomaterials to meet the diverse needs of medical applications, ultimately improving patient outcomes and quality of life.

5. Future scope

In the foreseeable future, additive manufacturing will be essential to producing implants that are specifically tailored to each patient's needs. As the need for implants grows, more attention will be paid to improving surface qualities with advanced coatings, particularly for materials like Ti6Al4V alloy that are meant to resemble real bone. As coating technology advances, new, biocompatible solutions suited to certain tasks will be created, offering efficient defence against immunological reactions. Furthermore, the creation of innovative coatings, such as multilayer binary, ternary nitride, and composite structures enhanced with osteoconductive qualities and medicinal compounds, has enormous promise for extending the life of implants, thwarting infections, and promoting bone growth. This path minimizes the possibility of rejection

Table 8
ASTM and ISO standards for assessing coating properties and thickness.

S. No	Property/ Parameter	ASTM Standard	ISO Standard
1.	Adhesion	ASTM D4541-Standard Test Method for Pull-Off Strength of Coatings Using Portable Adhesion Testers	ISO 4624 - Paints and varnishes Pull-off test for adhesion
2.	Nanoindentation Hardness	ASTM E2546 - Standard Test Method for Film Hardness by nanoindentation Test	ISO 14577 - film hardness by nanoindentation Test
3.	Corrosion Resistance	ASTM B380–18 Corrosion Testing of Decorative Electrodeposited Coatings by the Corrodkote Procedure.	ISO 11846:2015, Corrosion of metals and alloys for conducting cyclic corrosion tests for automotive coatings.
4	Thickness Measurement	ASTM B568–98, Nano/ micro range applicable to thin coatings.	ISO 14577–4, Testing in the nano/micro range applicable to thin coatings.
5	Scratch test	ASTM D7027–13, Scratch Resistance of Coatings	ISO 1518, Resistance of paints, coatings and varnishes by scratching with a hemispherically.
6	Wear	ASTM G99 - Standard Test Method for Wear Testing with a Pin-on-Disk Apparatus	ISO 7148 - Plain bearings - Testing of the tribological behaviour of bearing materials
7	Wettability	ASTM D7334 - Standard Practice for Surface Wettability of Coatings, Substrates and Pigments by Advancing Contact Angle Measurement	ISO 19403–2, Determination of the contact angle of liquid paints, varnishes and related products
8.	Biocompatibility	ASTM F981, F2382–18 - Standard Practice for Assessment of Compatibility of Biomaterials for Surgical Implants with Respect to Effect of Materials on Muscle and Insertion into Bone	ISO 10993–1 - Biological evaluation of medical devices - Part 1: Evaluation and testing within a risk management process

and places coated substrates, like Ti6Al4V, in a position where they blend in with normal physiological functions.

Coatings will become increasingly important as technology develops to protect patient longevity and well-being. The doping of materials can improve their durability and cost-effectiveness. Biocompatible doped coatings composed of high- and medium-entropy alloys have the potential to revolutionize biomedical applications. Micro-and nanostructured coatings are important biological response drivers that affect adhesion, differentiation, and cell behavior. The application of various fabrication techniques, including sol-gel and sputtering, will facilitate the creation of complex coatings and promote research and development in the biomedical field. The future of biomaterial surfaces will be shaped by these multidisciplinary technologies, which present exciting opportunities for additional studies and advancements.

6. Conclusions

In this study, biometals utilized in the biomedical industry are extensively presented, along with the diverse additive manufacturing processes employed for creating titanium alloys for biomedical applications. Notably, in recent years, there have been significant advancements in 3D printing additive manufacturing techniques for Ti6Al4V alloys in the biomedical field. Furthermore, the present study conducted a comprehensive review of the currently employed coatings aimed at modifying the surfaces of metallic biomaterials, encompassing a variety of biocompatible coatings. Subsequently, we explored surface modification through specific coatings, such as Nitride, DLC, HEA, metal oxide, and inorganic-polymer composites. The focus was on enhancing mechanical properties, degradation rate, corrosion resistance, and wear resistance crucial factors in advancing additive manufacturing for biomedical applications. Moreover, the effect of coating thickness on properties is substantial across various coating types, impacting mechanical strength, wear resistance, corrosion resistance, wetting behavior, and biocompatibility. Despite the distinct characteristics exhibited by different types of coatings, it is evident that each type possesses unique properties. The study underscores the coating of implants stands out as a strategic approach for improving biocompatibility and fostering osseointegration, all while preserving the integrity of the bulk material. Biomaterial coatings are highly beneficial for preventing bacterial colonization and promoting adhesion of tissue cells to the surface.

CRediT authorship contribution statement

Gurminder Singh: Writing – review & editing, Writing – original draft, Supervision. **ANKIT KUMAR:** Writing – original draft, Investigation, Conceptualization.

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.

Data Availability

The data that has been used is confidential.

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Appendix A. Supporting information

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