

Review

# Recent Developments in Coatings for Orthopedic Metallic Implants

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**Abstract:** Titanium, stainless steel, and CoCrMo alloys are the most widely used biomaterials for orthopedic applications. The most common causes of orthopedic implant failure after implantation are infections, inflammatory response, least corrosion resistance, mismatch in elastic modulus, stress shielding, and excessive wear. To address the problems associated with implant materials, different modifications related to design, materials, and surface have been developed. Among the different methods, coating is an effective method to improve the performance of implant materials. In this article, a comprehensive review of recent studies has been carried out to summarize the impact of coating materials on metallic implants. The antibacterial characteristics, biodegradability, biocompatibility, corrosion behavior, and mechanical properties for performance evaluation are briefly summarized. Different effective coating techniques, coating materials, and additives have been summarized. The results are useful to produce the coating with optimized properties.

**Keywords:** biomaterials; coatings; orthopedic implants; biocompatibility; biodegradability

## 1. Introduction

Many materials including polymers, metals, alloys, ceramics, and composites are used in orthopedic applications [1–5]. These materials are required to have excellent physical, mechanical, and tribological properties and must be non-toxic, biocompatible, and corrosion-resistant [6,7]. The most widely used materials for orthopedic applications are listed in Table 1. The problems with these conventional materials are their least biodegradability, biological inertness, similarity in properties to the bone, long-term stability, wear, and corrosion resistance [8–17]. The other issues related to these implant materials are stress shielding, secondary infections, metal ion release, etc [18–25]. Therefore, in most cases, multiple revisions are required in case of failure of implants. Moreover, the implants made of non-degradable materials often remain in the body up to their need. Hence, the non-degradability and long healing time demand revision surgery to replace or remove the implant after healing [26–29].

The fabrication of coatings on implant materials has become a topic of major interest to enhance the biological, tribological, antibacterial, and mechanical properties of orthopedics. The most important objective of implant material is to improve biocompatibility. The coating of bioactive material improves biocompatibility, prevents ion release from the metallic substrate which results in reduced mechanical failure. A high-quality coating should exhibit sufficient adhesion strength (50 MPa approved by US-FDA), high hardness of the final coat, excellent osseointegration, and osteoconduction properties, reduced cracks among the coating, and free of inclusions [30]. Another important feature is the degree of crystallinity which affects the solubility of the bioactive coating in the human body [30]. This article aims to review the impacts of coatings on the implant materials for the orthopedic prosthesis. The relative comparison of different coatings on metallic implant materials is reviewed systematically to choose the optimized coating properties.

**Table 1.** Most common biomaterials for orthopedic implants.

Material	Uses	Advantages	Disadvantages	Challenges
Titanium alloys [31,32]	Femoral hip stems Shoulder stems Fasteners, nails, rods, screws, wires Fracture fixation plates Pedicle screws and rods for spines	Lightweight Less biological response Biocompatible High corrosion resistance	Poor bending ductility Poor wear resistance Expensive High modulus	Biodegradable Biological inertness Antibacterial Stability in mechanical properties Wear reduction
Stainless steel alloys [33,34]	Plates, screws, pins, wires Sliding hip screws Flexible and intramedullary nails Cerclage cables	Widely available High ductility Accepted toughness Accepted biocompatibility	Very high modulus Allergic reactivity Stress shielding effect Poor wear resistance	Corrosion resistance Wear reduction Biological inertness
Cobalt-chrome Molybdenum [35]	Bearing surface in metal Plates and wires Shorter-term implants	Long term biocompatibility High corrosion resistance High wear resistance High impact durability	Stress shielding effect Poor machinability Biological toxicity due to release of Ni	Wear reduction Metallic fretting Biological inertness
Polyethylene/UHMWPE [36–38]	Bearing surfaces	Biocompatibility Wear resistance	Wear debris Lower mechanical properties Joint infections	Fatigue life
Alumina/ Zirconia composites [39,40]	Bearing surfaces	High smoothness Biocompatibility	High fracture rate	Brittleness

## 2. Coating Techniques

To enhance the efficacy of biomedical implants huge research has been carried out with a prime focus on developing techniques for coating or depositing bioactive materials on metallic substrates. Nowadays, researchers around the world are performing research on coating techniques to find the optimum processing parameters. There is further need for investigation on optimum adhesion between coating and substrate, development of methods for multilayers deposition to achieve different characteristics, and use of novel materials. The most common techniques that are recently used for coating metallic implant materials are listed in Table 2.

The physical vapor deposition (PVD) method includes different surface modifications such as evaporation, ion plating, and sputtering. The core idea behind these techniques is that a material is coated on a metal surface by initially vaporizing the material then letting it condense on a metal surface [41]. In orthopedics, sputtering is the most used method for coating metallic implant materials. Sputtering is usually carried out in the argon-rich environment in which gaseous argon is turned into positively charged vapors. These positively charged argon ions then collide with the metal substrate, generating reactive metal molecules. That bombard into metal and create a coating layer. In magnetron sputtering close magnetic field is used to control the ionization rate [42,43]. PVD is used to develop high purity and high dense bioactive coatings on implant materials with good adhesion strength. However, PVD is a time-consuming and expensive technique and produces a low crystalline layer that may be dissolved in the human body. Hence, further studies are needed to study the influence of PVD processing parameters on the crystallinity, porosity, and stability of bioactive coatings.

**Table 2.** Most common coating techniques for implant material coatings.

Coating Method	Method Classification	Advantages	Disadvantages
Physical vapor deposition (PVD) [44–53]	Cathodic arc deposition RF magnetron sputtering DC reactive magnetron sputtering Close field magnetron sputter ion plating Cathode plasma immersion ion implantation deposition Planar magnetron sputtering Electron beam evaporation	Coat complex geometries with ease High dense High purity Increased wear resistance	Delamination Expensive Time-consuming
Chemical vapor deposition (CVD) [54–56]	Atomic layer deposition Plasma assisted chemical vapor deposition	Coat complex geometries with ease Increased wear resistance	Delamination Expensive
Electrochemical deposition [57–63]	Electrophoretic co-deposition	Low temperature Increased wear resistance	Expensive Thin layer
Sol-gel [64–70]	Dip coating	Coat complex geometries High homogeneity High purity Low temperature Low cost	Low wear resistance Low permeability Delamination Low mechanical stability Thin layer
Plasma spraying [71–75]	—	Low cost Rapid deposition rate Long life span	Low adhesion Cracks Microstructure change
Micro arc oxidation [76–80]	—	Low cost Eco friendly Multifunctional coatings	Porosities formation Cracks Delamination

In the Chemical vapor deposition (CVD) technique, high temperature, high pressurized reactant gas is placed in a reactor which reacts with the metal surface to produce a thin coating on it [81,82]. CVD is capable to produce complex geometries, but a high initial cost is required for specialized equipment. Furthermore, the thickness and morphology of the coating can be changed by altering the precursor temperature in CVD. However, the coating produced by CVD showed delamination because of low adhesion and stability. Hence, comprehensive studies are needed to analyze the delamination or degradation mechanism of coatings before the application on orthopedic devices. In the electrochemical deposition process, a tightly adherent and thin coating of oxide, salt, or metal is deposited onto the substrate surface by electrolysis of a solution containing the metal ion or its chemical complex.

In the sol-gel method, a substrate is dipped into a colloidal suspension, and a gel layer is deposited onto the substrate surface. Then the excess liquid is removed by a drying process [83]. This method is widely used to create complex thin coating geometries with high homogeneity and purity. This method is used to coat metallic implant materials to enhance corrosion resistance. In addition, the sol-gel process is low-cost, which is used to maintain the parent mechanical properties of substrate because of the sol-gel nature and low processing temperature. However, this method has disadvantages as high permeability, low wear resistance, and cracking. The sol-gel process is sensitive to the coating material and the delamination occurs due to the difference in properties of substrate and coating material. Hence, further research is needed on substrate materials as the difference in thermal properties between the coating and the substrate cause delamination of coating and process failure. Hence, further research is needed to improve the degree of crystallinity and adhesion strength.

Plasma spraying is used to produce deposition rapidly with low thermal degradation as compared to other thermal coating techniques [84]. Presently, plasma-sprayed HA is the only coating approved by FDA [85]. Although this technique is effective to deposit HA coating on a metallic surface, it showed low crystallinity as increasing temperature disrupts the apatite layer. Moreover, this technique exhibits low adhesion strength and

cracks may be developed. However, more research is required to improve the quality of coating with better adhesion and durability. The research trend is to showcase improved efficacy, performance, and durability of biomedical implants because the contemporary technique is still not able to meet the desired goals.

A relatively plausible option for manufacturing a micro-porous, rough, and hard coating on metal substrates is micro-arc-oxidation (MAO). This method is inviting some serious attention as it could ensure significant adhesive characteristics between the coating and substrate. Secondly, researchers see it as a promising technique regarding the formation of a good crystalline coating with morphologies having a porous exterior. Furthermore, the said process is easy to operate, cost-effective, and environment-friendly. Fortunately, this method can produce multifunctional well as protective coatings by adjusting the processing parameters. However, this process and the characteristics of its final product depend on several factors. Most importantly, those factors include electric parameters, electrolyte composition, substrate material used, and geometry of the electrolytic cell. The complex interdependence of these factors makes this technique quite challenging. At the current level of our research, it would be unwise to draw some conclusions with certainty regarding the feasibility of MAO to produce hydroxyapatite coating without subsequent treatment. Furthermore, it has been observed that this process leads to the formation of porosities which can lead to corrosion and delamination. In addition, this method is not suitable to coat bioactive materials on metallic implants. So, further investigations are needed to resolve complications.

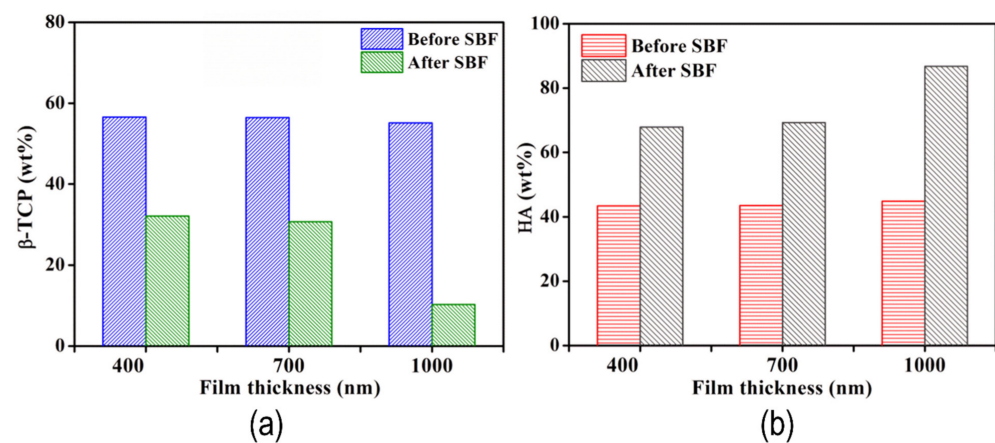
### 3. Coatings for Metallic Implants

#### 3.1. Coatings for Titanium

The most used titanium alloys for biomedical applications are Ti6Al4V and Ti6Al7Nb. These alloys are widely used in orthopedic applications because of their good corrosion resistance, high impact, fatigue strength, low density, inherent toughness, and lightness. However, their biological inertness shows some negative responses to cell and tissue behavior. So, both the new bone tissues and osteoblasts cannot grow well. Therefore, the bonding between host tissues and implants are not formed easily, which leads to poor osteointegration. As a result, Ti-based implant is detached from the host tissue in long-term implantation [86]. Another important cause of implant failure is an infection, which is caused by improper surgery, or bacterial activity in a physiological environment [87]. Hence, the ideal implant should be able to promote osteointegration, deter bacterial adhesion, and minimize prosthetic infections [88].

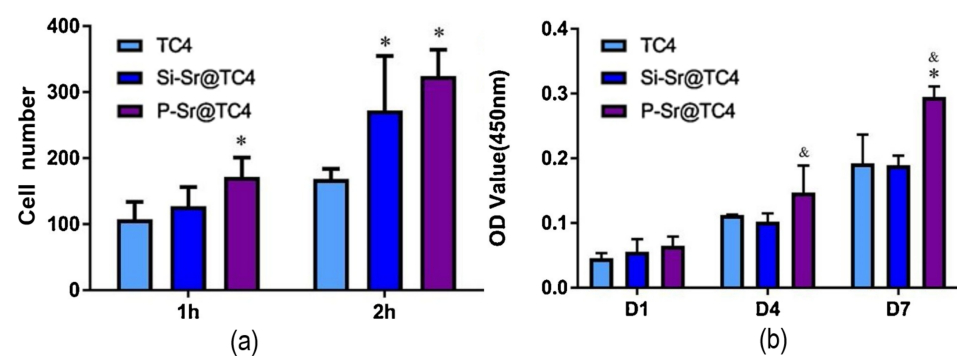
Several coating materials have been suggested for surface modifications of Ti implant material to enhance biocompatibility. Calcium phosphate-based biocompatible materials such as hydroxyapatite (HA), bioactive glass (BG), and biphasic calcium phosphate (BCP) are widely used for the replacement or repair of different implants due to their excellent biocompatibility, osteoconductivity, and osteointegration.

To enhance the biocompatibility of titanium, Behera et al. [86] deposited the BCP coating on Ti-6Al-4V and studied the influence of coating thickness on bioactivity, wettability, and mechanical properties. In vitro bioactivity of samples was evaluated by the formation of the apatite layer after immersion in SBF. The apatite film deposited on the surface of coated titanium provides the required surface chemistry for cell proliferation and adherence. Surface analysis confirms the formation of small elliptical and globular-like structures of apatite film on the coated titanium surface. Further, the wt.% of apatite layer enhances with the immersion time. The results of the study in terms of wt. % of HA and  $\beta$ -TCP over coated substrates before the immersion and after the immersion for 14 days are presented in Figure 1. Moreover, the phase analysis confirms the presence of HA peaks with no  $\beta$ -TCP phases. Therefore, it can be concluded that BCP-coated titanium samples exhibit good bioactivity due to the growth of apatite precipitation.



**Figure 1.** The weight percentage of (a)  $\beta$  TCP (b) HA of a film with different thicknesses. Reprinted with permission from [86].

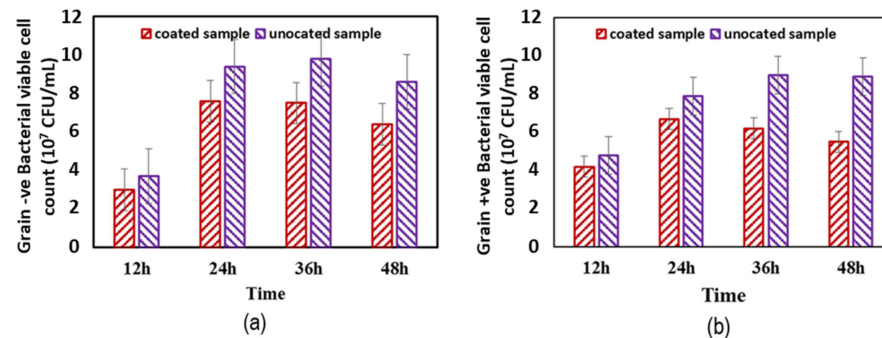
The undesirable bioactivity on the titanium surface such as lack of osteoinduction is a major contributing factor for the failure of implants. Li et al. [89] proposed that the incorporation of strontium (Sr) in calcium silicates and calcium phosphates can further improve the osteoinduction of orthopedic implants. The Sr-incorporated calcium phosphate (P-Sr) and Sr-incorporated calcium silicate (Si-Sr) on Ti alloy were prepared by micro-arc oxidation (MAO) and the biological properties of the two coatings were compared. The results in terms of cell adhesion and cell proliferation are presented in Figure 2. The cell number and OD values of coated and uncoated samples increased with incubation time. The results indicate that both coatings are effective to enhance corrosion resistance and promoting osteogenic differentiation ability. Both coatings not only can enhance the corrosion resistance and hydrophilic state of titanium (TC4) substrates but also promote bioactivity and osteogenic differentiation ability. In comparison to both coatings Si-Sr coating exhibit better biocompatibility.



**Figure 2.** Cell adhesion and cell proliferation response (a) Number of adhered cells (b) cell proliferation. (\* indicates statistical significance < 0.05 vs. TC4, & indicates statistical significance < 0.05 vs. Si-Sr@TC4). Reprinted with permission from [89].

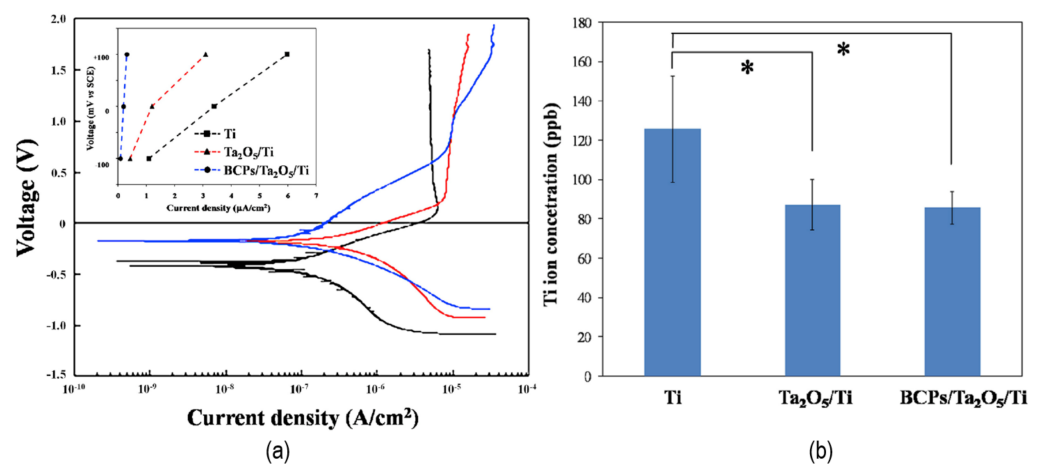
Li et al. [90] prepared the chitosan/HA coating on the titanium surface to improve the biological and antibacterial properties of titanium implants. First, the micro-nano structured HA coating was prepared on the titanium surface by micro-arc oxidation (MAO), and then the antibacterial agent of chitosan was loaded on the HA surface through the dip-coating method. The results showed that the obtained chitosan/HA composite coating accelerated the formation of apatite layer in SBF solution, enhanced cell adhesion, spreading, and proliferation, and it also inhibited the bacterial growth, showing improved biological and antibacterial properties. Although, with the increased amount of chitosan, the coverage of HA coating would be enlarged, resulting in depressed biological property, however, the antibacterial property was improved.

An antibacterial study is a necessary condition for an implant material because infectious adulteration is a prime source of concern during implant surgery. Hussein et al. [91] analyzed the antibacterial, biocorrosion, and mechanical performance of TiN coating on the titanium surface. Antibacterial activity was performed on TiN-coated titanium substrates against bacteria. The TiN-coated samples showed improved antibacterial properties as compared to uncoated samples due to the change in surface characteristics. The Ti surface exhibits higher sensitivity to bacterial adhesion due to the dissolution of oxide/passive films. The TiN coated surface exhibit antibacterial activity due to physical obstruction to the bacterial adhesion. The results of the study are presented in Figure 3.



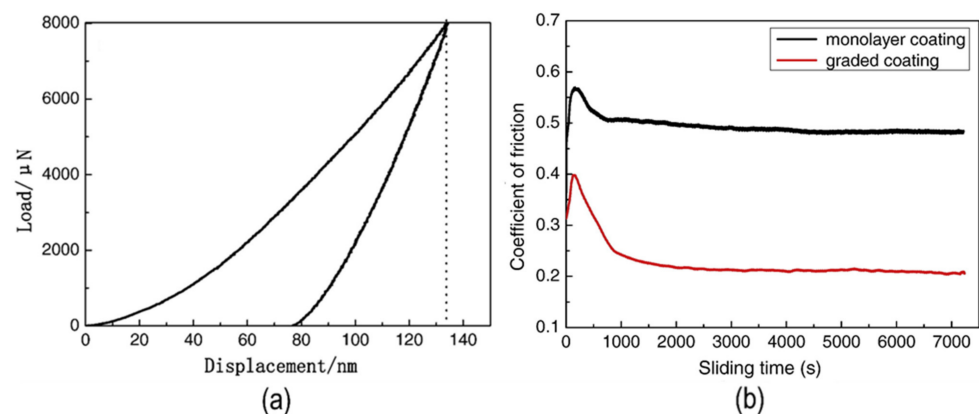
**Figure 3.** Bacterial viable cell count (a) gram -ve bacteria (*E. coli*) (b) gram +ve bacteria (*B. Subtilis*). Reprinted with permission from [91].

To improve the overall performance of orthopedic implants, it is essential to consider the other performance parameters including mechanical properties, corrosion, and wear behavior. The use of multi-coating materials can be effective to achieve the desired properties. And the investigation of these properties is essential in determining the implant performance. To improve the corrosion resistance with cytocompatibility and bioactivity, Sun et al. [92] deposited the multifunctional hybrid layer of BCP/Tantalum pentoxide ( $Ta_2O_5$ ) on the titanium surface. First, the  $Ta_2O_5$  layer was deposited on the titanium surface by the hydration condensation process. Then an electrochemical deposition method was used to deposit the BCP layer on the coated substrates. The results indicate that the  $Ta_2O_5$  improves the corrosion resistance while the BCP layer promotes surface bioactivity, hydrophilicity, and bone cell adhesion. In vitro electrochemical potentiodynamic polarization test was performed to evaluate the corrosion behavior of the coating surface. The results of corrosion tests are presented in Figure 4. The results show that the coated samples show lower corrosion potential as compared to untreated samples. The corrosion current densities of test samples were in following order: BCPs/ $Ta_2O_5$ /titanium ( $0.2 \mu A/cm^2$ ) <  $Ta_2O_5$ /titanium ( $1.2 \mu A/cm^2$ ) < titanium ( $3.5 \mu A/cm^2$ ). These results show that the presence of amorphous  $Ta_2O_5$  coating film decreased the current density of the titanium by approximately 65%, and the presence of crystalline BCP layer further decreased the current density of the  $Ta_2O_5$ /titanium by approximately 80%. Hence decreased current density and ion release due to the inner  $Ta_2O_5$  and outer BCPs layer of the titanium surface indicate the enhanced corrosion resistance.



**Figure 4.** Corrosion behavior of Ti, Ta<sub>2</sub>O<sub>5</sub>, and BCPs/Ta<sub>2</sub>O<sub>5</sub>/Ti samples (a) Corrosion current density (b) ion concentration. (\* indicates statistical significance  $p < 0.05$ ). Reprinted with permission from [92].

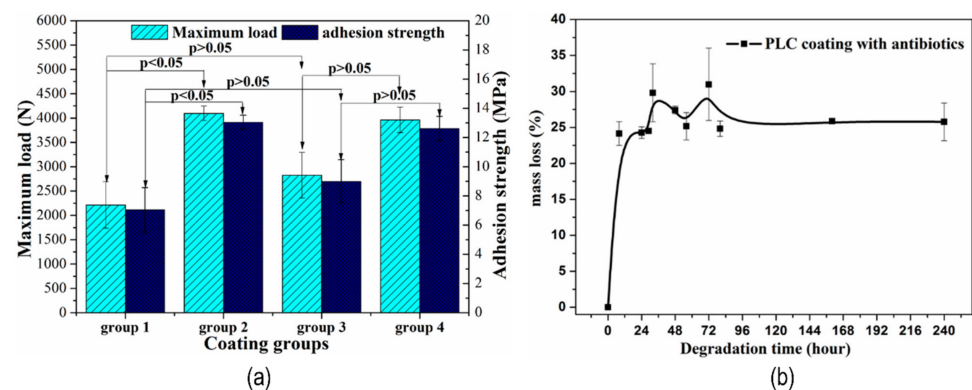
Several coatings have been produced on the titanium surface to enhance the wear resistance of the implant. Cui et al. [93] proposed the TiN coating for wear performance enhancement. The monolayer and graded TiN coatings were deposited on the titanium surface by DC reactive magnetron sputtering. The elastic modulus and hardness of coating specimens were measured under nano-indentation tests. The continuous and smooth curve suggests that the TiN coating exhibits good crack resistance. The results of the study are presented in Figure 5a. The ball-on-disc tests were performed to evaluate the wear performance of specimens in Hank's solution under the load of 10 N. The change of coefficient of friction (COF) with time under the sliding abrasion test is shown in Figure 5b. A 50% reduction in COF was observed for graded TiN coating as compared to monolayer TiN coating.



**Figure 5.** (a) Load-displacement response of graded coating (b) COF vs. sliding time response. Reprinted with permission from [93].

The adhesion strength and degradation behavior of coatings are important influencing parameters for performance analysis. Cao et al. [94] compared the four coating groups including Polylactide-L-lactide-CO-ε-caprolactone (PLC) coatings, PLC coating with antibiotics, micro-arc oxidation (MAO)/PLC double coating, and MAO/PLC double coating with antibiotics on titanium surface. The result shows that the use of MAO coating is very effective to increase the adhesion strength and load to failure of coating at the interface. The degradation test shows that the addition of antibiotics causes the loss of coating mass. The results of the study are presented in Figure 6. The study concludes that

the MAO/PLC double coating has a good potential for reducing the severity and incidence of implant-related early infections.



**Figure 6.** (a) Adhesion performance of various coating groups (b) degradation rate of coating of PLC coating. Adapted with permission from [94].

To minimize the stress shielding effect of titanium implants, the use of porous titanium implants instead of fully dense titanium implants has been reported in the literature. Moriche et al. [95] reported that porous titanium substrates exhibit lower mechanical properties, closer to those of human bones as compared to fully dense titanium substrates. Torres et al. [96] fabricated the porous titanium substrates and deposited the gelatin coatings on these substrates to improve the biocompatibility. Silver nanoparticles have been described to damage bacterial cells via prolonged release of  $\text{Ag}^+$  ions as a mode of action when immobilized on a surface [97]. To improve the antibacterial properties, Gaviria et al. [98] deposited the therapeutic Ag nanoparticles coatings on porous titanium substrates. The results showed that the coated porous titanium substrates exhibit lower antibacterial activity as compared to fully dense titanium substrates. As bioactive glass coating on titanium surface offers improved bioactivity and mechanical properties. So, Moriche et al. [95] evaluated the potential of bioactive glass coatings on porous titanium substrates. The results showed that bioactive glass-coated porous substrates exhibit improved mechanical properties with higher bioactivity due to the formation of a hydroxyapatite layer. Beltran et al. [99,100] coated porous titanium substrates with a bilayer of bioactive glasses to overcome the problems associated with titanium implants such as poor osseointegration and stress shielding.

The results of few recent studies are summarized in Table 3 and many other studies are reviewed to conclude the influence of coatings on titanium surface for orthopedic applications. Calcium phosphate-based coatings such as HA and BCP have been shown to induce bone formation and promote bone-implant integration [101–106]. The coated titanium become bioactive and biocompatible because of their surface characteristics due to the formation of the apatite layer. Unfortunately, poor mechanical performance has hindered these from becoming favorable coating materials. Most present studies have focused on incorporating different elements into HA or BCP coatings to improve mechanical or corrosion properties [107–113]. Few studies showed that the incorporation of tantalum (Ta), chitosan, Graphene-oxide (GO), and biodegradable metals, and  $\text{TiO}_2$  in HA or BCP is effective to achieve the required properties. Similarly introducing the inner layer is also effective to achieve the multifunction's of hybrid coatings [114–116]. The results show that these composites or multifunctional hybrid coatings are effective to improve biocompatibility, biocorrosion, and mechanical properties with the compromise of surface roughness and friction properties. Another challenge associated with these coatings is the adhesion strength which limits the use of these coatings on an industrial scale. Introducing the interface or seed layer can be helpful to improve the surface roughness and adhesion strength of calcium phosphate-based coatings [117].

The results in Table 3 show that many coating techniques have been employed to coat metal implant materials. Physical vapor deposition techniques including magnetron sputtering and cathodic arc physical deposition have been used effectively to achieve uniform distribution of bioactive glass, and TiN coatings with good adhesion strength and scratch resistance [86,93]. The grain size and microstructure of coatings can be controlled by controlling processing parameters. The processing parameters such as temperature, pressure, power, etc., are important to control the coating quality. Further optimization of these processing parameters can be effective to achieve high-quality coatings.

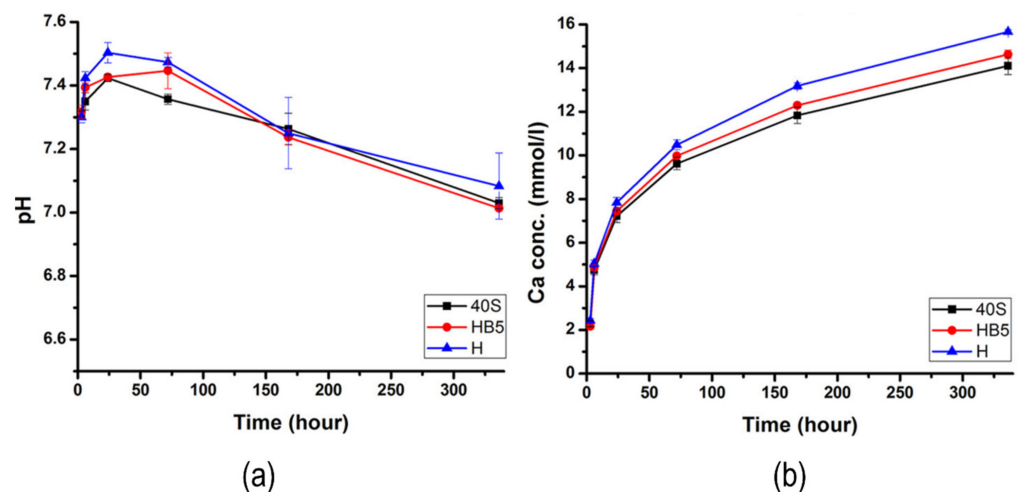
In comparison to HA and BCP coatings, TiN coatings showed improved corrosion, tribological, mechanical, antibacterial, and biological properties. The significant enhancement in all-determining parameters can be easily observed from tabular data for TiN coated specimens. Particularly, TiN coating is beneficial to enhance the mechanical properties up to 3 to 7 times. As per the data of two studies the hardness increased above 7 times as compared to the uncoated titanium surface. As another study showed that the hardness increased 4 times for TiN coated specimens. The data of these three studies showed that the elastic modulus of TiN coated specimens increased 2 to 4 times as compared to uncoated specimens. The corrosion tests showed that the corrosion current density of TiN coated specimens is very low as compared to uncoated specimens. The mean TiN coating showed good corrosion resistance. The tribological results showed a significant reduction in (up to 50%) COF and wear rate for TiN coated specimens. The biocompatibility tests show that the TiN coatings are biocompatible to some extent and better than uncoated titanium specimens. The bacterial studies show that the TiN coating exhibit antibacterial properties. Hence the results showed that the TiN coatings fulfill the required criteria for orthopedic applications. But before the use of these coatings, degradation studies are needed to be conducted for the long-term time. Further, the durability of TiN coating is needed to be investigated in long-term vitro and vivo studies. The studies on other coating materials including diamond-like carbon, Polylactide-L-lactide-CO- $\epsilon$ -caprolactone (PLC), TiTaHfNbZr, etc. are still insufficient, and results of such coatings are not attractive to perform more studies on these coating materials.

**Table 3.** Summary of results for coatings on titanium surface.

Ref.	Coating Material	Thickness	Coating Method	Biocompatibility/Antibacterial Properties	Corrosion/Degradation Behavior	Mechanical Results	Tribological Results
[86]	Biphasic calcium phosphate (BCP)	1000 nm	RF magnetron sputtering	wt.% of HA—86.76% Enhancement in wt.% of apatite layer show bioactivity	—	Microhardness—455 HV (140%)	Roughness—153 nm (168%) Higher scratch resistance
[92]	BCP/Ta <sub>2</sub> O <sub>5</sub>	1 μm/700 nm	Electrochemical deposition/Hydration condensation	Spherical apatite layer formation in immersion test show bioactivity	Corrosion current density—0.2 μA/cm <sup>2</sup> (5.7%)	—	—
[94]	Micro-arc oxidation & Polylactide-L-lactide-CO-ε-caprolactone (PLC)	5.4 μm	Micro-arc oxidation/dip coating	—	Mass loss—24.8%	Adhesion strength—13 MPa Load to failure—4000 N	—
[118]	Ti-TiN-TiAlN	2.52 μm	Close field magnetron sputter ion plating	—	Corrosion current density—1.74 × 10 <sup>-3</sup> μA/cm <sup>2</sup> (7.5%)	Hardness—37.2 GPa (775%) Elastic modulus—409 GPa (339%) Adhesion strength—48 N	COF—0.23 (50%) Wear rate—3.73 × 10 <sup>-5</sup> mm <sup>3</sup> /Nm (7.53%)
[93]	TiN	5.8 μm	DC reactive magnetron sputtering	Relative growth rate of cells—+90% OD values and Hemolysis ratio show good biocompatibility.	—	Elastic modulus—281 GPa Hardness—0.8 GPa Bonding Force/Adhesion strength—80 N	COF—0.2 Wear rate—0.62 × 10 <sup>-6</sup> mm <sup>3</sup> /Nm Wear track depth—0.34 μm
[91]	TiN	5 μm	Cathodic arc-physical deposition	Antibacterial inhabitation efficiency rates—138.2%	Corrosion current density—3.21 × 10 <sup>-2</sup> μA/cm <sup>2</sup> (0.35%)	Hardness—38.3 GPa (726%) Elastic modulus—358 GPa Indentation depth—600 nm (47.69%)	Roughness—13 nm COF—0.448 Contact stress at failure—2.23 GPa
[89]	Sr incorporate calcium phosphate	5–8 μm	Micro-arc oxidation	Better cell adhesion and cell proliferation	—	—	—
[119]	Bioactive glass (BGF18)	—	—	Similar cell adhesion Thicker biofilm growth for coated (128%)	—	—	Surface roughness—3.96 nm (1320%)
[120]	TiTaHfNbZr	—	RF magnetron sputtering	—	—	Hardness—3.46 GPa Elastic modulus—115 GPa	Roughness—2.78 nm (327%) COF—0.15
[121]	Flourine doped diamond-like-carbon/Si	1.6 μm	Cathode plasma immersion ion implantation deposition	—	—	Hardness—18.3 GPa Elastic modulus—163 GPa	Roughness—7.8 nm COF—0.11

### 3.2. Coatings for Stainless Steel

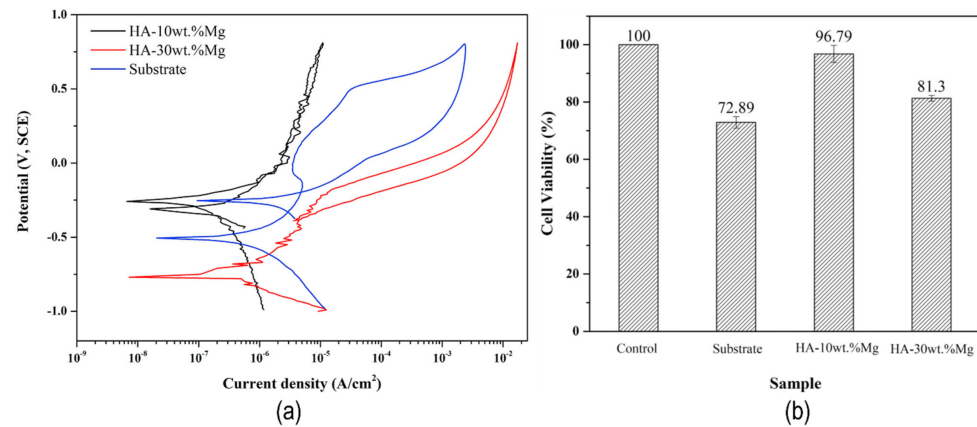
Stainless steel is the most used material because of its low cost and high mechanical properties. Therefore, it is still used for making many orthopedic implant components like fixation screws, bone plates, etc. However, stainless steel is the least biocompatible and anticorrosive, and it does not integrate with bone naturally and might release some toxic ions and corrosion products. The metal implant encapsulated by body tissues released ions into the body which can become the cause of loosening and failure of the implant. A coating of bioactive materials on the stainless steel is a practical solution to induce osteointegration by decreasing or suppressing the released products. In addition, these coatings should be antibacterial. Several bioactive and antibacterial coatings have been used for stainless steel implants. Many investigations have been carried out to improve the biocompatibility, biocorrosion, and antibacterial properties of stainless steel by depositing BG or composites coatings containing BG [122–128]. BG-coated stainless-steel implants provide better integration to the body tissues by forming apatite at the coated metal surface. Furthermore, they can inhibit or regulate corrosion in the physiobiological environment [129]. To improve the further biocompatibility, antibacterial, and corrosion properties various materials including silane, chitosan, silica, gelatin, polyether ether ketone (PEEK), Zein, a natural fibroblast and copper, etc. have been added in BG to make composites coatings. Cuevas et al. [130] prepared the HA-loaded BG coated stainless steel substrates, and then evaluated their bioactivity in SBF solution. The thickness of the apatite layer and released ions concentration in the immersion test were observed for coated specimens. The results show that the addition of HA in BG is effective to increase the thickness of the apatite layer. The thickness formation rate at the start of soaking was higher, while a significant reduction in growth rate was observed after the 5 days of soaking. Furthermore, ion release behavior in the immersion test was the same for all types samples. Al-Rashidy et al. [131] used the electrophoretic co-deposition technique to coat stainless steel with three different BG compositions and studied the corrosion behavior. The achieved coatings were homogeneous, uniform, and crack-free. The pH change and the concentration of calcium ions were measured in the immersion test. The decrease in pH and increase in released Ca ions were observed due to the formation of HA crystals on the substrate surface. The results shown in Figure 7 showed that all the BG coating layers have a better ability to form HA crystal on their surface.



**Figure 7.** (a) pH change (b) Ca ion concentration in SBF solution for different compositions of BG coatings on stainless steel. Reprinted with permission from [131].

The deposition of the HA layer on stainless steel is also effective to enhance the bioactivity and corrosion resistance of stainless-steel implant materials. Rezaei et al. [132] deposited the HA-10wt.%Mg and HA-30wt.%Mg coating on the stainless steel for biomedical implants. The objective of the intermediate layer was to improve corrosion resistance

while Mg particles were added to improve the osseointegration process by forming porosities in the physiological environment. The results of the study are presented in Figure 8. The results show that the HA-coated samples exhibit lower corrosion current densities and higher cell viability as compared to uncoated samples.



**Figure 8.** (a) Corrosion potential (b) Cell viability. Reprinted with permission from [132].

The results of different coatings on stainless steel are summarized in Table 4. The studies revealed that the HA and BG both are suitable coating materials to enhance the corrosion, bioactivity, and antibacterial characteristics. Such coatings exhibit weaker adhesion and still, there is needed to improve the adhesion strength. Poor adhesion between metallic and coating interface leads to failure and unsuitable for high load-bearing applications. Poor crystallized formation on metallic implant material caused the coating to dissolve and decrease adherence to a metallic surface. The failure occurs at the interface in case of long-term use. Therefore, the stability of HA and BG coatings are the most important factors to determine the success of steel implants. Several additive materials such as gelatin, PEEK, polyvinyl alcohol (PVA), etc. have been added in BG to improve the adhesion. So, there is needed to improve the adhesion stability and degradation behavior of coatings.

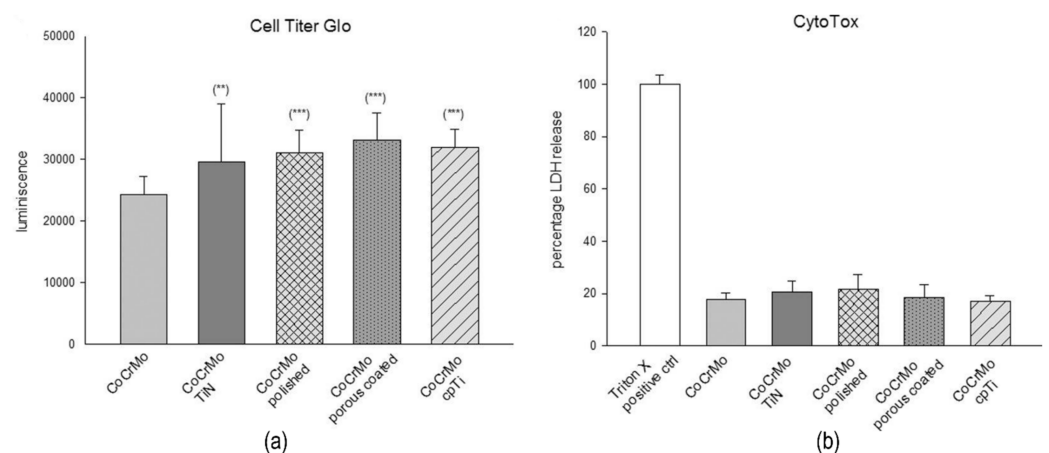
### 3.3. Coatings for Cobalt-Chrome Molybdenum (CoCrMo) Alloys

CoCrMo alloys exhibit favorable bioactivity with good corrosion and mechanical properties. Therefore, these alloys are widely used in orthopedic applications, especially for manufacturing knee and hip implants. Many methods have been employed to improve biocompatibility and other properties. Despite the high corrosion resistance of CoCrMo alloys due to the presence of thin oxide film, dangerous ions like Ni, Co, Cr are released in the body from CoCrMo prosthesis components. The elevated concentration of these ions may lead to the inflammatory response and implant failure after the joint implantation.

Table 4. Summary of results for stainless steel.

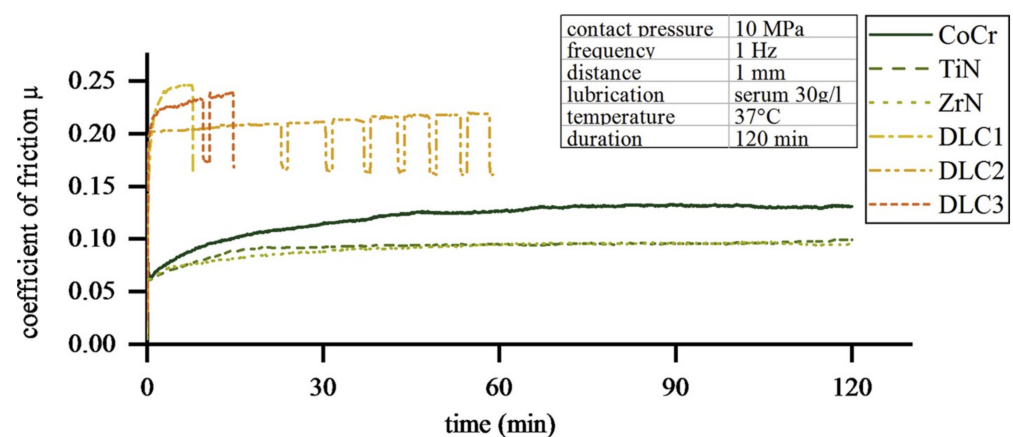
Ref.	Coating Material	Thickness	Coating Method	Biocompatibility/Antibacterial Properties	Corrosion/Degradation Behavior	Mechanical Results	Tribological Results
[131]	Bioactive glass-chitosan	143 $\mu\text{m}$	Electrophoretic co-deposition	—	pH—7.4–7.9 Ca ion concentration— $20 \times 10^{-2}$ mmm/h Corrosion current density— $20.93 \mu\text{A}/\text{cm}^2$ Corrosion rate—5.02	—	Roughness—170 $\mu\text{m}$ (2.9%)
[133]	Bioactive glass/silane	2/0.6 $\mu\text{m}$	Dip coating	Optical density—0.2	Corrosion current density— $154 \mu\text{A}/\text{cm}^2$	Show no detachment	—
[134]	HA-3SiC	45 $\mu\text{m}$	Electrophoretic deposition	—	Corrosion potential—0.041	Elastic modulus—728 MPa Bonding strength—1.61 MPa	—
[135]	Bioactive glass/silane	1.2 $\mu\text{m}$	Dip coating	—	Improvement in corrosion resistance but show degradation in immersion test	—	—
[132]	HA-10wt.%Mg	100 $\mu\text{m}$	Plasma spraying	Cell viability—96.7% (132%) Distribution of calcium phosphate show bioactivity	Mg ion concentration—71 ppm Corrosion potential—−0.250 Corrosion current density— $0.12 \mu\text{A}/\text{cm}^2$	—	—
[136]	Carbon nano tubes (CNTs)	80 $\mu\text{m}$	FEM	—	—	Static stress—87.574 MPa (181%)	—
[137]	Chitosan-20 Polyvinyl alcohol (PVA)-BG	—	Electrophoretic deposition	HA forming ability show best bioactivity	Corrosion potential—−0.7265	Optimum adhesive strength for 20 wt. % PVA coating	—
[138]	ZNO	220 nm	Atomic layer deposition	—	Corrosion potential—−0.131 Corrosion current density— $0.04 \mu\text{A}/\text{cm}^2$	Indenter load to failure—0.85 N	Surface roughness—0.40 $\mu\text{m}$
[139]	Amorphous carbon: Niobium	2 $\mu\text{m}$	Planar magnetron sputtering	—	Enhancement in corrosion protection	Hardness—16.5 GPa Young modulus—44 GPa	COF—0.10
[140]	5 Ag-Sr-Chitosan-Gelatin	—	Electrophoretic deposition	Suitable proliferation of osteoblast cells Antibacterial	—	Suitable adhesion strength	—
[141]	Ag-CaSZ nanocomposites	—	E-beam evaporation	Hemocompatible Calcite precipitation	Improved corrosion resistance	—	—

Leonberger et al. [142] performed the surface modifications on a CoCrMo alloy surface to improve the biocompatibility of these alloys. Five different CoCrMo substrates including uncoated, TiN coated, polished, porous polished, and pure Titanium (cpTi) coated were compared in terms of cytotoxicity and cell viability, and their osteoblast potential was evaluated. The cell viability test showed the evenly spread of cells on all the modified surfaces. All modified samples showed increased cell viability and the highest cell viability was observed for TiN coated alloy as shown in Figure 9a. The cytotoxicity test showed no significant changes as shown in Figure 9b. Lactate dehydrogenase (LDH) is released from the disrupted membranes. The membrane is disrupted in necrotic cells and LDH is released from the cell. The LDH release remained stable for all substrates. Hence, the TiN coatings showed good compatibility and prevent the CoCrMo surface from encountering the tissues. Furthermore, TiN coated specimens showed good corrosion resistance and reduced the released ions from CoCrMo base material.



**Figure 9.** (a) Cell viability ( $p < 0.01$  \*\*;  $p < 0.001$  \*\*\*) (b) CytoTox LDH release. Adapted with permission from [142].

Doring et al. [143] deposited the TiN, ZrN, and diamond-like carbon (DLC) coatings on CoCrMo alloy and performed the friction and wear studies. The lower values of coefficient of friction (COF) were recorded for TiN coated substrate as shown in Figure 10. The low COF of about 0.094 is attributed to the very smooth surface achieved by cathodic arc deposition.



**Figure 10.** Friction results for different coated materials. Reprinted with permission from [143].

The results of different studies are summarized in Table 5. The results showed that HA, TiN, and TiSiN coatings exhibit better performance as compared to other listed coatings.

**Table 5.** Summary of results for CoCrMo alloys.

Ref.	Coating Material	Thickness	Coating Method	Biocompatibility/Antibacterial Properties	Corrosion/Degradation Behavior	Mechanical Results	Tribological Results
[144]	HA/oxide	12.73/51.03 $\mu\text{m}$	Sol-gel dip coating	—	—	Adhesion strength—8.63 N Increases by increasing sintering temperature.	—
[142]	TiN	5.5 $\mu\text{m}$	Physical vapor deposition	Osteoblast viability—145.6%	—	Tensile strength—22 MPa Shear strength—20 MPa	Roughness—50 $\mu\text{m}$
[145]	Fluorohydroxyapatite	6.22 $\mu\text{m}$	Sol-gel procedure	Corrosion potential—0.264 V Corrosion density— $3.7 \times 10^{-3}$ $\mu\text{A}/\text{cm}^2$	—	Show high adhesion	Roughness—0.477 $\mu\text{m}$
[146]	Tantalum	1.5 $\mu\text{m}$	Magnetron sputtering	—	—	Multilayered Ta film shows best adhesion	—
[147]	TiSiN	1.89 $\mu\text{m}$	Cathodic arc evaporation	—	Reduction in fretting volume—1000 times Reduction in Co Ion release—90%	Elastic modulus—396 GPa Hardness—41.6 GPa Residual stress—−8.00 GPa Critical load—0.329 N	Roughness—0.0406 $\mu\text{m}$
[147]	ZrN	2.37 $\mu\text{m}$	Cathodic arc evaporation	—	Reduction in fretting volume—10 times Reduction in Co Ion release—90%	Elastic modulus—409 GPa Hardness—29.3 GPa Residual stress—−8.00 GPa Critical load—0.175 N	Roughness—0.0134 $\mu\text{m}$
[148]	Graphene	5.76 $\mu\text{m}$	Chemical vapor deposition	Improved cell proliferation	—	Adhesion strength—1152 $\mu\text{N}$	—
[143]	TiN	1.7 $\mu\text{m}$	Cathodic arc evaporation	—	—	Hardness—30 GPa Penetration modulus—514 GPa Critical load—10 N	Roughness—0.0045 $\mu\text{m}$ COF—0.094 Wear rate— $4 \times 10^{-15}$ $\text{m}^3/\text{mN}$
[143]	Diamond-like carbon	0.7 $\mu\text{m}$	Cathodic arc evaporation	—	—	Hardness—74 GPa Penetration modulus—680 GPa Critical load—3 N	Roughness—0.0285 $\mu\text{m}$ COF—0.023
[149]	TiNbN	3–6 $\mu\text{m}$	Physical vapor deposition	Viability—above 100%	Reduction in Co/Cr/Mo ion released—80.1/62.5/48%	—	—
[150]	TiN	2 $\mu\text{m}$	Plasma assisted chemical vapor deposition	—	Corrosion rate—0.793 $\mu\text{m}/\text{y}$	—	—

#### 4. Conclusions

Titanium, stainless steel, and CoCrMo alloys are the most widely used biomaterials for orthopedic applications. The most common causes of orthopedic implant failure after implantation are infections, inflammatory response, least corrosion resistance, mismatch in elastic modulus, stress shielding, and excessive wear. To address the problems associated with implant materials, different modifications related to design, materials, and surface have been developed. Among the different methods, coating is an effective method to improve the performance of implant materials. In this article, a comprehensive review of recent studies has been carried out to summarize the impact of coating materials on metallic implants. The antibacterial characteristics, biodegradability, biocompatibility, corrosion behavior, and mechanical properties for performance evaluation are briefly summarized.

Many coating techniques such as physical vapor deposition, chemical vapor deposition, electrochemical deposition, sol-gel, plasma spraying, and micro-arc oxidation have been used in recent years to coat metallic implants. Among these techniques physical vapor deposition techniques including cathodic arc deposition, DC reactive magnetron sputtering, close field magnetron sputter ion plating, etc. are effective techniques to produce the coating with improved biocompatibility, corrosion resistance, and mechanical properties. A significant enhancement in performance is reported for several coating materials including HA, BG, and TiN. However, the stability, adhesion, and degradation performance of these coatings are challenges and limiting the use of these coatings on an industrial scale.

Many recent studies showed that the incorporation of tantalum (Ta), chitosan, Graphene-oxide (GO), and biodegradable metals, and TiO<sub>2</sub> in HA or BCP is effective to achieve the required properties. Similarly introducing the inner layer is also effective to achieve the multifunction's of hybrid coatings. The results show that these composites or multifunctional hybrid coatings are effective to improve biocompatibility, bio-corrosion, and mechanical properties. In comparison to HA and BCP coatings, TiN coatings showed improved corrosion, tribological, mechanical, antibacterial, and biological properties.

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