metals

MDPI

Review

Modifying Coatings for Medical Implants Made of Titanium Alloys

Sergey Grigoriev [1], Catherine Sotova [1], Alexey Vereschaka [2,*], Vladimir Uglov [3] and Nikolai Cherenda [3]

[1] Department of High-Efficiency Machining Technologies, Moscow State University of Technology "STANKIN", Vadkovsky Lane 3a, 127055 Moscow, Russia; s.grigoriev@stankin.ru (S.G.); e.sotova@stankin.ru (C.S.)
[2] Institute of Design and Technological Informatics of the Russian Academy of Sciences (IDTI RAS), Vadkovsky Lane 18a, 127055 Moscow, Russia
[3] Department of Solid State Physics and Nanotechnology, Belarusian State University, Nezavisimosti Ave. 4, 220030 Minsk, Belarus; uglov@bsu.by (V.U.)
* Correspondence: dr.a.veres@yandex.ru

Abstract: This review considered various methods for depositing special modifying coatings on medical implants made of titanium alloys including techniques such as electrochemical deposition, sol–gel process, atmospheric plasma deposition, and PVD methods (magnetron sputtering and vacuum arc deposition). The rationale is provided for the use of modifying coatings to improve the performance efficiency of implants. The concept of a functional multilayer coating designed for products operating in the human body environment is proposed. The advantages and disadvantages of various methods for depositing coatings are considered based on the possibility of their use for obtaining modifying coatings for medical purposes deposited on a titanium alloy base.

Keywords: modifying coatings; titanium alloys; implant

check for updates

Citation: Grigoriev, S.; Sotova, C.; Vereschaka, A.; Uglov, V.; Cherenda, N. Modifying Coatings for Medical Implants Made of Titanium Alloys. *Metals* **2023**, *13*, 718. https://doi.org/10.3390/met13040718

Academic Editor: Asit Kumar Gain

Received: 9 March 2023
Revised: 31 March 2023
Accepted: 5 April 2023
Published: 6 April 2023

1. Introduction

One of the main challenges in regenerative medicine is the treatment of diseases and injuries associated with violation of skin integrity and loss of large fragments of bone, cartilage, and other tissues. Along with cell therapy and the introduction of biologically active substances, the use of special implants [1–3] is often relevant in the case of the extensive damage of body tissues.

The manufacturing of implants designed to restore the functioning of damaged body tissues applies materials that are able to form an oxide film, which provides them with good biotolerant properties [4]. As a rule, metal materials are used to restore bone tissue as well as to fasten bones, and polymers are applied for soft tissues.

Metal implants are actively used in various fields of medicine (e.g., osteosynthesis, dentistry, endoprosthetics, etc.), and have a number of advantages including the required combination of physical and mechanical properties, low weight, good resistance to corrosion, relatively low cost, biocompatibility (they are non-toxic and not rejected by the human body), durability, ability to initiate the process of osseointegration, flexibility, and elasticity.

Titanium (Ti) and its alloys are used as the main materials in the manufacturing of bone implants [5–15]. These materials are characterized by high durability with low density as well as high elasticity, which is five times higher than that of human bones [16]. Furthermore, titanium is typically classified as a bioinert material. Back in 1965, Swedish research professor Per-Ingvar Brånemark discovered the process of osseointegration (i.e., the growth of bone substance on titanium surfaces [17]). The implantology most often uses the following titanium alloys [12–15,18]:

- In accordance with the standards of ISO 58321 II [19] and ASTM F 67-89 [20], Grade 1–4 titanium alloys contain about 99% titanium (Ti) and up to 0.5% iron (Fe);

- Grade 5 (Ti–6Al–4V alloy) is an alloy of titanium (Ti) (88%) with aluminum (Al) (up to 6.75%) and vanadium (V) (up to 4.5%). Grade 5 is 3.0–3.5 times more durable than Grade 4 and is cheaper to manufacture [21]. The mentioned high durability makes Grade 5 titanium alloy irreplaceable in the manufacture of thin reliable implants with special compression or aggressive threads to be installed in dense basal regions of jawbones. However, the presence of vanadium in Grade 5 titanium alloy may slow down the process of osseointegration.

However, the elastic moduli (60–120 GPa [22]) of second-generation Ti alloys are significantly higher than those of human cortical bone (mainly 10–20 GPa) [23]. The difference in the modulus of elasticity of the implant and bone tissue leads to bone atrophy [24] and loosening of the implant with damage to the bone tissue [25], and consequently, to an increase in the likelihood of secondary fractures after restoration [26], since most of the stress is absorbed by the alloy due to its higher modulus of elasticity [24,25]. In this regard, research continues the development of titanium alloys for medical applications, which are currently largely focused on the so-called third generation β-models, which have elastic moduli close to those of human bones. This type of titanium alloy is free of harmful or allergenic elements such as vanadium and nickel. Thus, the Ti–28Nb–35.4Zr alloy [27] was developed, which was subjected to thermal exposure for one hour at 890 °C followed by cold deformation. As a result of such thermomechanical treatment, a homogeneous structure was formed, consisting of a β-phase, while the tensile strength of the alloy was 633 MPa, and the elastic modulus was 63 GPa. In addition, the authors of [27] suggested that the presence of an α-phase can reduce the value of the elastic modulus, since they are able to dissolve a higher content of β-stabilizers.

The Ti–35Nb–7Zr–5Ta alloy is also known, which has favorable biological activity and a low elastic modulus (50 GPa) [28] as well as the Ti–24Nb–4Zr–8Sn alloy, the elastic modulus of which is only 45 GPa, the tensile strength is 850 MPa, in addition, it has a high corrosion resistance [29,30] due to the formation of passivating films of TiO_2 and Nb_2O_5 and a little of ZrO_2 and SnO_2 on the surface [8].

Ti–Mo alloys are also widely used as biomedical materials [31–33], however, when implanting products from these alloys in vivo, infection around the implant and protection of the bone tissue from stresses occur [34] (the causes and consequences of this are discussed above). To eliminate these problems, these alloys are additionally alloyed with other components to reduce the modulus of elasticity of the alloy (bringing it closer to the modulus of elasticity of bone tissue) as well as to impart antibacterial properties to the alloy.

For example, in the study by [35], β-titanium alloy of the Ti–12Mo–10Zr type was used. Additional alloying with zirconium made it possible to reduce the value of the elastic modulus (~50.8 GPa) while maintaining a sufficiently high compressive yield strength of the alloy (~430.89 MPa).

In the study by [34], Ti–15Mo–xCu (x = 3, 7, 11, and 15 wt.%) alloys with an integrated functional structure were obtained by powder metallurgy using Ti, Mo, and Cu powders as starting materials. The results showed that Ti–15Mo–xCu alloys mainly consist of β-Ti, α-Ti phases as well as Ti_2Cu intermetallic particles located along the α-Ti grain boundaries. At the same time, the strength of the Ti–15Mo–xCu alloys decreased with increasing Cu content. With a Cu content of 11 wt.%, the Ti–Mo–Cu alloy showed a higher compressive strength of 318.8 MPa and the lowest elastic modulus of 5.2 GPa. In this case, the antibacterial activity of the alloy can be controlled by the concentration of released Cu ions, which, in turn, is proportional to the Cu content. Thus, for the Ti–15Mo–11Cu alloy, it is possible to obtain antibacterial indices of S. aureus and E. coli over 95% with good cytocompatibility.

Another way to improve osseointegration and reduce the toxicity of Ti–Mo alloys is to dope them with yttrium (Y). Ti–15Mo–xY alloys (x = 0.5, 1.0, 1.5 wt.%) [36] were studied, the hardnesses of which were 405, 435, and 510 HB, and the ultimate compressive strength was 17.82, 18.04, and 18.14 MPa, respectively. The increase in mechanical properties with

the introduction of yttrium and an increase in its concentration in Ti–Mo alloys is associated with the deoxidation of the titanium matrix and the strengthening effect of Y oxides.

Promising alloys for the production of orthopedic implants are the Ti–Si alloy, which showed greater cell proliferation and osteoblastic protein expression as well as a better biological profile compared to commercial pure Ti [37].

In addition, the use of biomaterials with a porous structure can reduce the elastic modulus of the titanium alloy and promote its osseointegration. Thus, the formation of a porous structure is facilitated by the introduction of the TiH_2 modifier into the composition of the sintered alloy of the Ti–Si–Zr system to activate sintering [38]. It has been observed that the degree of porosity is affected by the amount of TiH_2 and the particle size of TiH_2 affects the pore size. In this case, with the introduction of fine TiH_2 particles, the dependence of the elastic modulus of the Ti–Si–Zr alloy on the fraction of TiH_2, and with the introduction of large TiH_2 particles, porosity did not significantly affect the elasticity modulus.

The use of titanium implants may sometimes provoke complications associated with the phenomenon of metallosis. This problem may be caused by the accumulation of metal ions from the composition of implants in the soft tissues of the human body, which leads to intoxication of the body as well as damage and destruction of the implants themselves. The phenomenon of metallosis is one of the key problems in osteosynthesis [39–41]. When installed in body tissues, implants are subjected to various kinds of influences including compression, stretching, torsion, displacement, and bending. As a result, the implants are subject to deformation with a change in the internal crystal structure of the metal. Thereby, all processes proceed in the aggressive biological environment, which may be described as an electrolyte with a large amount of chlorine (Cl) and hydrogen (H) ions [42]. As a result, complex electrochemical redox reactions take place on the implant surface with the formation of various compounds and the generation of galvanic currents, which actively affect the surrounding tissues [43]. The prolonged use of metal implants may provoke disturbances in the oxidative reactions in the surrounding tissues and symptoms of general intoxication.

In [18,44], the studies found that vanadium contained in titanium alloys has a toxic effect on biological objects. At the same time, although aluminum and iron are not toxic elements, they affect the formation of the connective tissue structure around the implants and cause extensive tissue contamination. Iron also inhibits the growth of organic culture. Furthermore, the tissue cell adhesion to the implants made of titanium alloys is slightly lower than to implants made of pure titanium [45].

Protective, usually oxide, films (coatings) are formed on the surface of the implants in order to reduce the release of metal ions into the body tissues. However, with the prolonged contact of implants with a biological environment, the oxide films become damaged and cease to perform their barrier functions, thus ultimately leading to the need to remove the implant [46–51].

Another complication that may occur with the implantation is inflammatory processes as well as expansion between the implant and the bone tissue of the so-called film infection caused by a conglomerate of microorganisms whose cells are attached to each other. This infection is inaccessible to the effects of antibiotics and antiseptics delivered by the bloodstream [52].

Conceptually, prosthetic elements introduced into the human body are foreign bodies (*corpora aliena*), and they may cause a corresponding reaction of the immune and other systems of the human body. In [53], it was noted that the main onsets of osteosynthesis stability disorders appear in the expansion of aseptic necrosis and lysis of the bone tissue around an implant. The presence of metal prosthetic elements in the human body may contribute to the expansion of an inflammatory process in the implant area, especially after infectious diseases as well as due to various types of immunodeficiency disorders [54]. In particular, it was noted that, according to the studies carried out in [55], mild inflammation, stopped by the antimicrobial therapy, was detected for 13 out of 110 patients (11.8%), and severe inflammation, which required the removal of implants, was diagnosed for

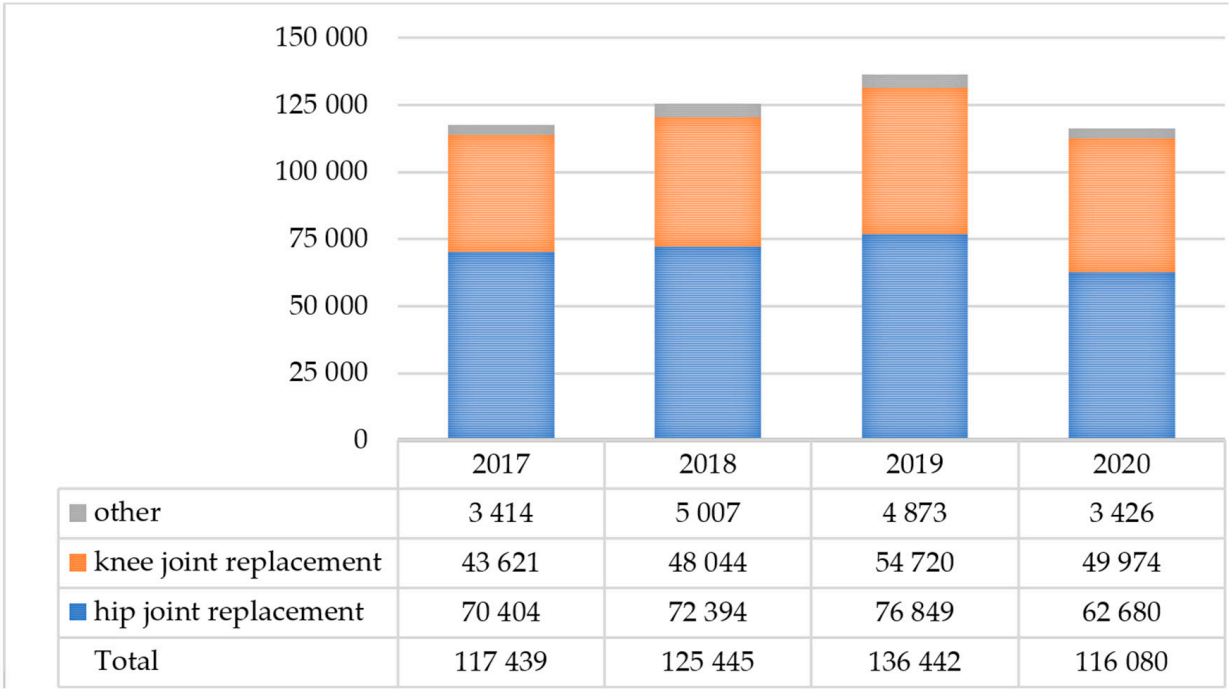
32 patients (29.1%). Suppuration of soft tissues in the implant area during the treatment of patients with bone fractures was observed for 12.7–22.0% of patients, depending on the nature of prosthetics [56].

The general observations presented in [56] (the installation of several thousand implants) found that cases of suppuration in the implant area were diagnosed for almost 17.0% of patients and amounted to 66.9% of all complications detected in them. According to the studies conducted by the Russian Scientific Research Institute of Traumatology and Orthopedics (RSRI of TO), named after R.R. Vreden (Moscow, Russia), during the treatment of 728 patients, inflammation and suppuration in the areas of implants were diagnosed for 19.0% of patients [56]. It is the phenomenon of metallosis that is the main (in 40% of cases) reason for the need to replace a knee joint implant [41]. Thereby, the time period between the primary implantation and the onset of metallosis ranges from 6 weeks to 26 years [41]. In 2014, in the United Kingdom, the phenomena of metallosis and other complications resulted in the need for the replacement of 10% of hip joints and 7% of knee joints previously implanted [57,58]. In 2020, in the United States alone, 498,000 hip joint replacement and 1,065,000 knee joint replacement surgeries were performed, and by 2040, the number may increase to 1,429,000 hip joint and 3,416,000 knee joint replacement surgeries [59].

The latest data in the Russian Federation on arthroplasty refer to 2020 and were published in the form of a report by N.N. Priorov [60]. Figure 1 shows data on the number of joint replacement surgeries in adult patients performed in 2017–2020 in the Moscow region of the Russian Federation. In 2019, 136,442 joint replacement surgeries were performed in adult patients including 76,849 hip replacement surgeries (56.3%) and 54,720 knee joint replacement surgeries (40.1%); other limb joint replacement surgeries (shoulder, elbow, ankle joints, small joints of the hand) amounted to 4873 operations (3.6%). During 2017–2019, the number of operations progressively increased, where the growth was 16.2%. In 2020, according to [60], 116,080 joint replacement surgeries were performed. The number of operations decreased by 15% compared to 2019, which may be due to the SARS-CoV-2 pandemic and a decrease in the number due to restrictions on elective operations. Endoprosthesis replacement of the hip joint was performed in 62,680 cases (54%), the knee joint in 49,974 cases (43%), and other in 3426 cases (3%). The structure of joint arthroplasty operations in patients older than the working age was similar. The number of joint replacement surgeries in persons older than working age (84,441) was 72.7% of the total number of joint replacement surgeries in adults (116,080). From 2017 to 2019, in patients older than the working age, there was also an increase in the number of operations: from 82,860 to 103,213 (by 24.6%), and in 2020, a decrease in the number of operations to 84,441 (by 18.2%). The structure of joint replacement operations in patients older than working age in 2020 (Figure 2) was as follows: hip joint—43,209 operations (51.2%); knee joint—39,319 (46.6%); other—1913 operations (2.2%) [60].

Thus, the number of joint replacement surgeries conducted due to the phenomena of metallosis and similar complications may be measured in hundreds of thousands per year throughout the world. The data presented indicate the need to find ways to overcome the undesirable phenomena of complications.

The modification of the surface properties of the implant material with coatings deposited using various methods is not only able to significantly reduce the risk of the onset and expansion of the above described complications, but it also significantly accelerates the healing process [61]. Therefore, in [62], it was found that a nitride coating has protective properties and prevents the migration of toxic ions (in particular, ions of vanadium) from an implant into body tissues. In addition to their barrier functions, coatings can also act as an activator and catalyst of regenerative processes [63–66].



	2017	2018	2019	2020
other	3 414	5 007	4 873	3 426
knee joint replacement	43 621	48 044	54 720	49 974
hip joint replacement	70 404	72 394	76 849	62 680
Total	117 439	125 445	136 442	116 080

Figure 1. Number of joint replacement surgeries in adult patients performed in 2017–2020 in the Moscow region in the Russian Federation.

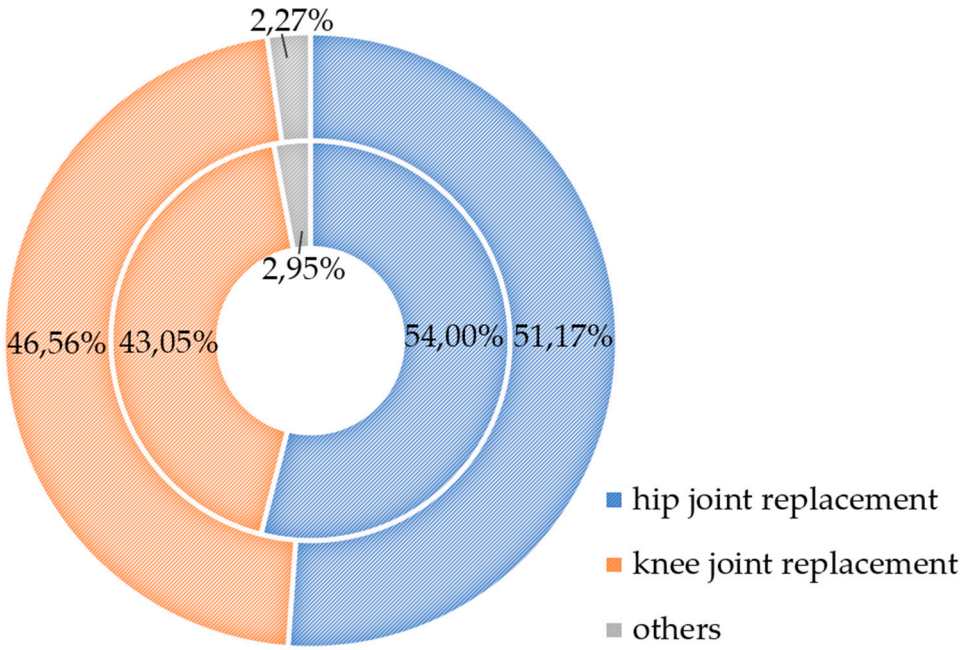


Figure 2. The structure of joint replacement operations in 2020 in the Russian Federation (outer ring—the number of joint replacement surgeries in adult patients; inner ring—the number of joint arthroplasty operations in persons older than working age).

Thus, the improvement in the performance properties of implants designed for various purposes can be achieved by the modification of their surface properties through the deposition of multifunctional coatings. These coatings perform barrier functions and may also have a structure and contain bioactive additives that promote the regeneration of body tissues.

The relevance of this direction is confirmed by the growing number of scientific articles that present the results of studies related to the modification of the surface properties of titanium implants (Figure 3). When analyzing the results of a search query for the keywords (titan* AND implant*) and (coating* OR (surface AND modificat*) in the Scopus bibliographic database in the period from 1989 (the year of registration of the first patent for a titanium implant) to the present, 11,968 publications have been identified, while over the past 10 years, their total number has more than doubled (from 5002 to 11,968).

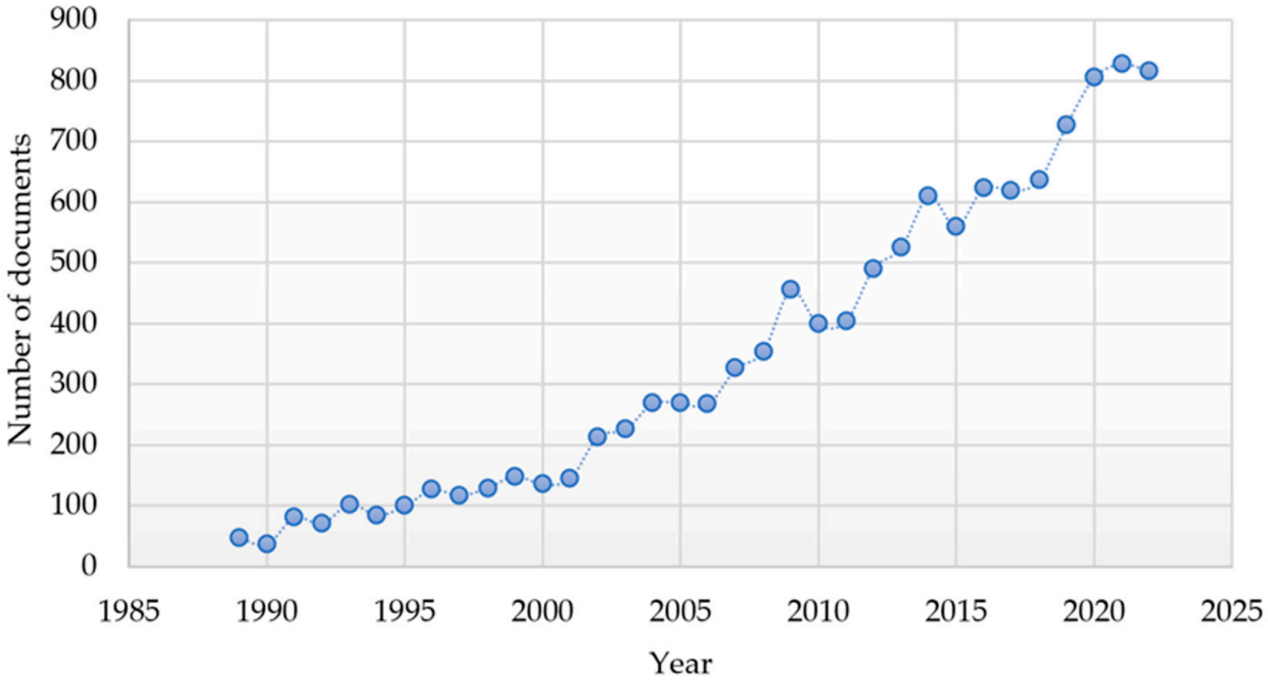


Figure 3. Analyzed search results of publications for the keywords (titan* AND implant*) and (coating* OR (surface AND modificat*)) from 1989 (the year of registration of the first patent for a titanium implant) to the present (according Scopus).

Figure 4 presents a word cloud built using the keywords of the above-mentioned sample, limited to the time period of the last five years (from 2018 to the present), and keywords were also selected that only related to titanium substrate compositions and modifying coatings. According to the presented results, the Ti4Al6V alloy remains the traditional material for titanium implants. At the same time, to improve the osseointegration of these products, barrier coatings of TiO_2 (anodic oxidation) and/or TiN (PVD methods) have mainly been applied as well as bioactive coatings of hydroxyapatite (deposition technologies are different) or sol–gel coatings of various composition containing bioactive additives. However, it is worth noting the growing interest in new types of substrates, new compositions of titanium alloys Ti–Nb–Zr, Ti_β–Nb–Ta–Zr, and Ti–Sr, while coating compositions become more complex: multilayer, multicomponent, reinforced nanotubes of TiO_2 [67,68], Ag/TiO_2 [69], $SrTiO_3$ [70], and others. In addition, the functionality of the coatings is also expanding, and the number of studies aimed at improving not only the biocompatibility of titanium implants, but also giving them antibacterial properties in order to reduce postoperative inflammatory processes is increasing, for which various Ag [71], Cu [72], and Zn [73] compounds are introduced into the coatings, and polymer layers are formed that include antibiotics (gentamicin [74], vancomycin [75], chitosan [76], and others).

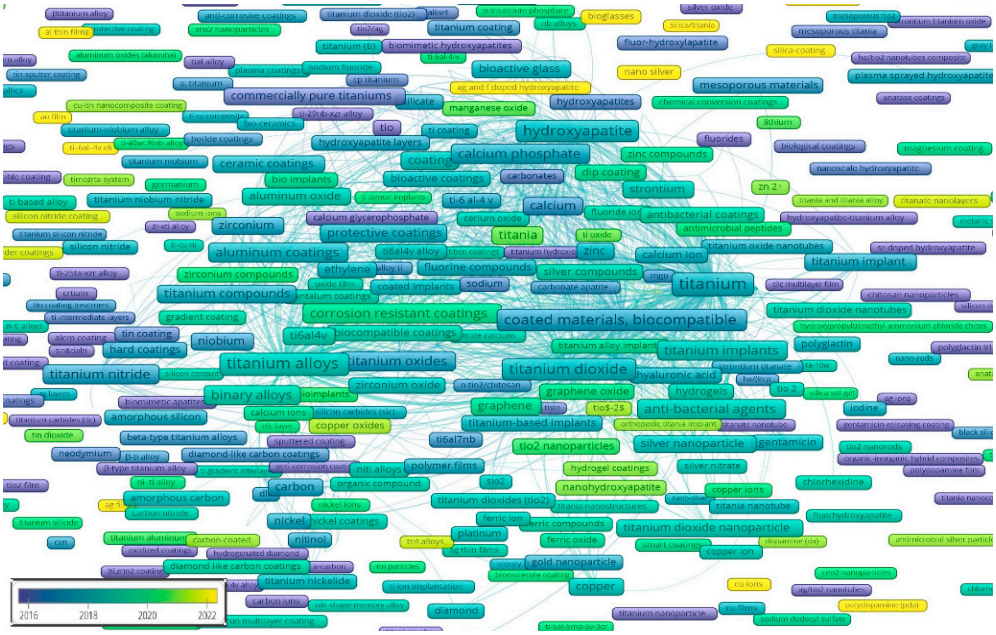


Figure 4. Word cloud based on keywords of publications for the keywords (titan* AND implant*) and (coating* OR (surface AND modificat*)) from 2018 to the present (according Scopus).

2. Methodological Base for Implant Surface Modification

Composite structures are increasingly used in various areas of modern manufacturing. Figure 5 considers a conceptual diagram of a similar structure as applied to critical medical devices that operate in the biologically active environment of a living organism, in particular, implants.

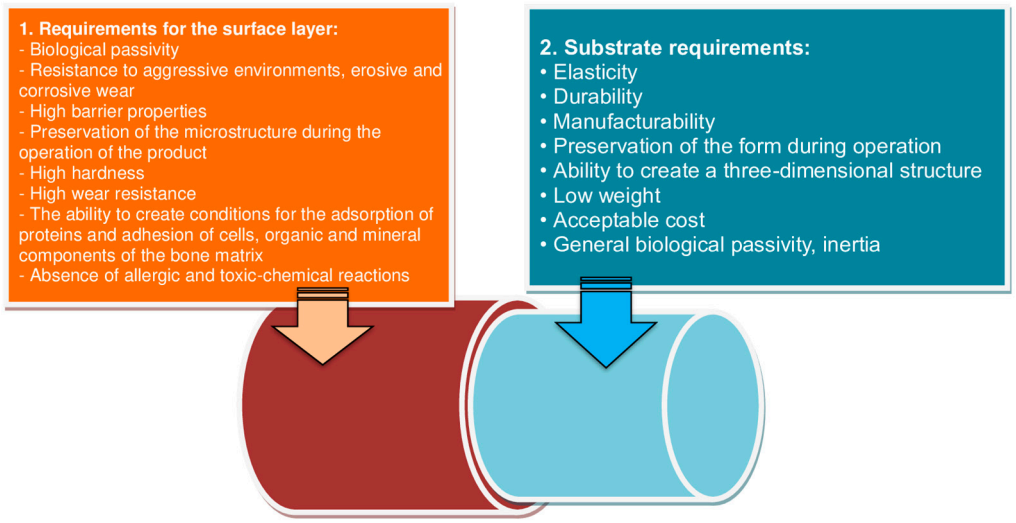


Figure 5. Concept of the compositional structure of critical medical devices operating inside the human body.

On one hand, implants should have the following properties:

- Elasticity, durability, manufacturability, preservation of the form during the operation, ability to create a three-dimensional structure;
- Low weight;
- Relatively low cost;
- General biological passivity, and chemical inertness.

On the other hand, among the requirements for implant surface properties, the following may be distinguished, in particular:

- Selective (portioned) biological activity (in particular, bactericidal properties to be manifested for a limited period of time after direct implantation procedure);
- Resistance to aggressive environments, erosive and corrosive wear;
- Properties of a barrier between the implant material and the human body tissues;
- Preservation of the microstructure during the operation of the product;
- High hardness and wear resistance;
- Favorable conditions for the absorption of proteins and adhesion of cells, organic and mineral components of the bone matrix;
- Absence of allergic and toxic-chemical reactions.

The above list, which can be expanded for each individual case, demonstrates that many properties are in fact conflicting (e.g., elasticity and durability/high hardness, biological activity/passivity, compliance with high requirements at an acceptable cost, etc.) Accordingly, it is practically impossible to find a material that would meet all of the above-listed requirements at the same time. The best way to meet the challenge is to use composite materials.

The modern manufacturing of various medical products use single-layer coatings most often. While such coatings are able to significantly improve the performance properties of implants, their capabilities are limited due to their inherent constraints. Based on the concept of the phenomenological role of the coating as an intermediate medium between the contacting materials of any interacting pair ("metal–metal", "metal–non-metallic medium", "solid–liquid/gas medium", etc.) [77–84], it can be assumed that the best combinations of the properties are provided by surface structures (modifying coatings) consisting of three layers, each of which has its clearly defined functional purpose. Figure 6 depicts the conceptual diagram of a multilayer modifying complex (coating) consisting of three functional layers.

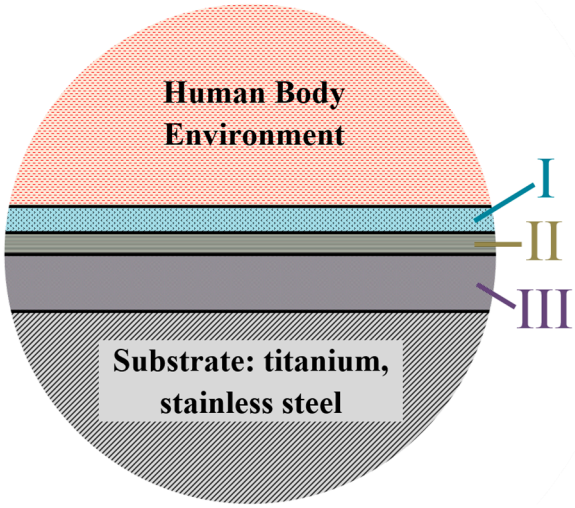


Figure 6. Conceptual diagram of a multilayer modifying complex.

I—**Outer layer** in direct contact with the human body tissues, which:

- May have antibacterial properties (for example, it may contain silver nanoparticles, have micro- and nanoporous structures with possible filling of pores with dosed components of antibacterial action or accelerating the healing process);
- May promote the absorption of proteins and adhesion of cells, organic and mineral components of the bone matrix;
- Should guarantee the absence of allergic and toxic-chemical reactions;

- May be partially lost during the operation (due to the reactions involving biologically active components).

II—**Intermediate layer**, which:

- May act as a base for the outer layer, providing high adhesion with it and creating conditions for its successful formation;
- May have high resistance to wear and erosion;
- May perform barrier functions and be characterized by high biological passivity;
- May provide a smooth transition of properties from the adhesive layer to the outer layer, including due to its gradient structure;
- May have high values of hardness and wear resistance, which can be provided by the application of multi-component (high-entropy) systems, characterized by minimization of the free energy of formation due to the maximum possible configurational component of their entropy.

III—**Adhesive layer**, which provides the following functions:

- High adhesion between the modifying complex (coating) and the substrate;
- High corrosion resistance, barrier properties, biological passivity;
- Gradual transition from the substrate to the intermediate and outer layers.

The analysis of the results of scientific research on the tasks of improving the performance properties of titanium implants by the deposition of modifying coatings has found that there is a clear current trend toward an ever wider use of multilayer coatings.

The below consideration is focused on the main compositions of the modifying coatings used in the manufacturing of medical implantable devices and methods for their deposition.

3. Modifying Coatings Used to Improve the Performance Properties of Titanium Implants

3.1. Coatings Produced by the Electrochemical Deposition Method

The formation of coatings by the electrochemical deposition method has long been widely used in medicine [85–87]. This method consists of depositing material on a conductive surface of a substrate by passing current through a liquid medium in contact with it, which contains chemical elements of the material being deposited. Along with its relative simplicity and low cost, the electrochemical deposition method also has a number of significant drawbacks including a high level of environmental pollution, danger to personnel, need to use complex treatment facilities, etc. It is practically impossible to control the structure and properties of the coatings during their deposition. It is also not possible to create modifying complexes with a multilayer architecture. In addition, it should be noted that the coatings obtained by the electrochemical deposition method are characterized by relatively low hardness and wear resistance and have high porosity. The latter is rather a positive property in the case of the formation of implant surface microrelief. The presence of microdefects on the implant surface increases the contact area and allows osteogenic cells to attach to the implant surface with the help of structural proteins and glycoproteins, thereby promoting the process of osteogenesis [88,89].

The electrochemical deposition method is most often used to form an oxide film (of titanium dioxide) on the implant surface. The film is bioinert and performs a barrier function. In [90], it was found that the surface modification of the Ti–Zr alloy by its anodizing enhanced early osseointegration in comparison with mechanically treated implant surfaces. In [91], the authors found that the anodic oxidized surface had inherent photocatalytic activity that was able to enhance the process of osseointegration. Another in vitro study [92] proved that an anodized surface reduced the adhesion of *Streptococcus mitis* compared to a machined surface.

The advantages of the anodized surface of the implant contribute to its better stabilization. The anodized surface is more suitable for implantation in complicated conditions

as well as in the presence of relative contraindications to implantation such as diabetes mellitus, smoking, periodontal disease, and others [93].

In addition, the process of anodizing makes it possible to obtain a hydrophilic surface with a surface tension above 30 dynes/cm, which interacts more closely with biological fluids, cells, and tissues, and accordingly, enhances the process of osseointegration. Therefore, in [93], the authors proved the superiority of a hydrophilic anodized surface in the early stages. In the postoperative time periods of 4, 8, and 12 weeks, the indicators of hydrophilic implants were consistently higher than those of the control group (implants with the hydrophobic surface of RBM, Resorbable Blast Media, i.e., after sandblasting) and SLA (Sandblasted Largegrid, Acid-Etched, i.e., combined processing including sandblasting with acid etching). The above may be explained by the fact that the hydrophilic surface stimulates the active growth of bone tissue on the entire implant surface, which results in rapid mechanical stability.

In [94], the consideration focused on a coating in the form of a microporous oxide structure with the inclusion of calcium and phosphorus deposited by the plasma electrolytic oxidation (PEO) method on Ti–6Al–4V titanium alloy. After the coating had been deposited, the implant surface exhibited high wettability and a surface free energy value, which is favorable for cell attachment.

The coating of $TiO_2/CaSiO_3$ for titanium implants was considered in [95]. The layer of TiO_2 was deposited by the method of plasma electrolytic oxidation, and the layer of $CaSiO_3$ by the method of electron beam evaporation. According to the results of the studies, the deposition of $CaSiO_3$ significantly increased the possibility of the formation of apatite on the nanostructured coating of TiO_2 in the simulated body fluid. Meanwhile, MG63 cells on the coating of $TiO_2/CaSiO_3$ demonstrated higher proliferation and viability rates than those on the coating of TiO_2.

In [96], a biocompatible coating of Ti–Zn–PO_4 was formed on a titanium substrate by hydrothermal treatment in an acidic solution of zinc phosphate at 250 °C for 10 h. The adhesion of the coating to the substrate was (48.3 ± 9.2 MPa). An in vitro cell study found that the results of cell proliferation for the layer of Ti–Zn–PO_4 were much better than those for the uncoated titanium substrates.

The above-described method has a significant limitation, which consists of an extremely narrow range of compositions of the coatings, which mainly act as a barrier for the release of metal ions from the substrate. To create a multilayer structure, it is necessary to involve additional technological processes (in particular, change of electrolytes), while the substrate should be electrically conductive, which significantly complicates the process and increases its cost. In addition, the adhesion between the layers will not be very high in such cases.

3.2. Coatings Produced by the Sol–Gel Method

The sol–gel process is a technology for obtaining materials, in particular, nanomaterials including the production of sol with its subsequent transfer to a gel, that is, a colloidal system consisting of a liquid dispersion medium enclosed in a spatial grid formed by the combined particles of the dispersed phase [85,97–101]. This method makes it possible to achieve a uniform distribution of elements of the multi-component systems over the surface of various solids. Moreover, the synthesis process is relatively simple and provides excellent control over the composition of the coating as well as their deposition on surfaces of almost any shape.

In [102], the authors examined the coating of SrO–SiO_2–TiO_2 obtained by the sol–gel immersion method and deposited on an ultrafine-grained alloy substrate of $Ni_{50.8}$–$Ti_{49.2}$. The electrochemical testing in simulated body fluid (SBF) proved that the pitting potential was increased from 393 mV (SCE) for the uncoated sample to 1800 mV (SCE) for the SrO–SiO_2–TiO_2-coated sample and that the corrosion current density decreased from 3.41 μA/cm^2 to 0.63 μA/cm^2, respectively. The testing also detected an increase in osteoblast-like cell attachment and their expansion in comparison with the uncoated sample.

In [103], hydroxyapatite (HA) coatings were deposited by the sol–gel method on substrates made of porous titanium–niobium alloy (Ti–6Al–7Nb). Good adhesion was detected between a HA coating and titanium substrates due to the mechanical interaction and possible chemical bonding. Application of HA coatings deposited by the sol–gel method contributed to the prevention of the release of metal ions and bioactivation of the surface. This coating demonstrated excellent chemical stability and increased the resistance to corrosion of titanium products at oblique bone ingrowth.

Another advantage of the use of sol–gels as coatings is their ability to locally deliver a wide range of antimicrobials such as antibiotics at a controlled rate. In [75], the authors studied the effect of synthesis parameters on the properties of thin sol–gel films containing antibiotics (vancomycin) on a substrate of Ti–6Al–4V. It was found that the thickness of the coating (its weight) and the corresponding dose of vancomycin in the coating increased in proportion to the number of layers. An in vitro study demonstrated sustained (up to 2 weeks) release of vancomycin from thin sol–gel films, while the rate of vancomycin release and film degradation may be adapted to therapeutic needs by controlling the sol–gel treatment parameters (i.e., number of layers and drug concentration in the layer). In addition, the study proved the possibility of the formation of a multilayer coating with layers containing different concentrations of vancomycin.

Thus, the use of the sol–gel method makes it possible to produce bioactive coatings for various purposes with a controlled rate of degradation and removal of active substances.

3.3. Coatings Produced by the Air Plasma Spraying (APS) Method

The method of air plasma spraying (APS) implies that material (powder) of the future coating is being fed into a plasmatron, heated to melting, and transported to the surface by a plasma stream. This method is used to produce metal, ceramic, or plastic coatings. The advantage of the air plasma spraying method lies in the possibility of producing coatings of various compositions at atmospheric pressure [104,105].

During the coating deposition, a small amount of amorphous silicon dioxide (SiO_2, ~1, 2, 5 wt.%) was introduced into the HA suspension, which was then spray-dried with a powder [106]. The raw material powder was sprayed onto a substrate of the Ti–6Al–4B alloy using the air plasma spraying technology.

The high velocity suspension flame spraying (HVSFS) method was used to deposit 45S5 bioactive glass on a titanium substrate [107]. This coating did not exhibit cytotoxicity, and human osteosarcoma cells were able to well adhere and multiply on its surface.

A biocompatible glass-ceramic coating was developed based on silicon (Si), carbon (C), and nitrogen (N) of the SiOCN–Pateks system as well as a technology for depositing it to dental implants of the Ti–6Al–4V alloy by the plasma enhanced chemical vapor deposition (PECVD) method [108]. The Pateks coating is safe for the fibroblast monolayer and does not inhibit the respiratory processes in them. The application of a Pateks glass-ceramic coating (0.5 μm thick) reduced the content of aluminum and vanadium ions in the model medium by almost 2 times and provided a barrier that reduced the negative biological effect of these ions on peri-implant tissues. An in vivo study found a reduction in the time of bone tissue compaction around the experimental coated titanium implants.

In [109], the study considered the effect of plasma modification of the surface of a pure titanium implant on its corrosion resistance in simulated biological fluids (SBFs) and artificial saliva (SAGF medium) as well as on the microbial adhesion of *P. gingivalis (Porphyromonas gingivalis)*. After the plasma modification, numerous formations of reactive oxygen species (ROS) were observed on the surface of the material and the wettability of the product improved. In comparison with the control group, the corrosion resistance of the treated products was higher and the absorption of bacterial suspension was significantly lower than in the control group on the third and fifth day ($p < 0.05$). Thus, the electrochemical and microbial corrosion resistance of titanium may be improved by depositing coatings using the APS method.

A technology of atmospheric argon plasma sputtering (AAPS) on pure titanium substrates was developed and a composite coating with a hydroxyapatite content of 20 wt.% was deposited [110]. As a result, a dense composite coating with a typical HA morphology homogeneously distributed in a titanium matrix was produced; HA decomposition during the plasma spraying process was prevented. The adhesion strength is significantly higher for titanium-reinforced HA coatings than that for regular HA coatings, and their friction properties are comparable to those of a titanium substrate. The higher corrosion current of the HA/Ti composite compared to that of the pure titanium coating in the simulated body fluid (SBF) indicates good bioactivity of the composite coating, which is also testified by the formation of an apatite layer during an in vitro test. The obtained results testify to the good potential of HA/Ti composites as materials for the implants operating under mechanical loading conditions.

In [111], to improve the corrosion resistance and biocompatibility of titanium alloys of the Ti–Mo–Si system, ZrO_2 coatings were deposited by atmospheric plasma spraying on Ti15Mo, Ti15Mo0.5Si, Ti15Mo0.75Si, and Ti15Mo1.0Si substrates, which were obtained on equipment for vacuum arc remelting (MRF ABJ 900) from high purity powders: Ti (99% purity), Mo (99% purity), and Si (99% purity). The morphology of the coatings was shown to be uniform, without microcracks, while the presence of β-Ti and ZrO_2 phases with a tetragonal crystal structure was observed, while zirconia is very stable in simulated body fluids and does not adversely affect the bone healing process. The instantaneous corrosion parameters (parameters of instantaneous corrosion) of samples coated in Ringer's solution had very good values (for example, the corrosion current for coated samples on Ti15Mo, Ti15Mo0.5Si, Ti15Mo0.75Si, and Ti15Mo1.0Si substrates was 3.033, 2.131, 4.458, and 3.963 A/cm^2, respectively), while the oxide layer on the surface protects the alloy from the aggressive absorption of electrolytic media. The results of the study also showed that the coating contributed to a decrease in the elastic modulus of the coated samples (51.71 ± 0.1 GPa for Ti15Mo0.5Si-ZrO_2 and 48.27 ± 0.2 GPa for Ti15Mo-ZrO_2) by 2 times compared with the titanium elasticity modulus (103–120 GPa), bringing it closer to the biological bone elasticity modulus (10–30 GPa), which makes it possible to avoid implant stress screening by bone tissue [111].

3.4. Coatings Deposited by the Magnetron Sputtering Method

The method of magnetron sputtering is widely used to form nitride and oxide barrier coatings [112–123].

In [112], the investigation focused on the effect of the coatings containing titanium dioxide and silver (TiO_2/Ag) and zinc oxide (ZnO) on the antibacterial activity of a titanium implant against *Streptococcus mutans* and human gingival fibroblasts (HGF). It was found that the antibacterial activity of the ZnO coating was higher than that of TiO_2/Ag coating. However, in terms of biocompatibility, the products coated with ZnO were inferior not only to the products coated with TiO_2/Ag, but also to the uncoated (control) samples. At the same time, according to the data of the MTT assay (colorimetric assay for measuring cell metabolic activity), the average values of optical density (OD) for the samples coated with TiO_2/Ag after 72 h were similar to those obtained for the uncoated Ti sample.

The (Zr,Ti)CN coating deposited on Ti–6Al–4V was studied. The coating thickness was 1.8–2.1 μm, and the hardness was 25–29 GPa [113]. During the testing of the samples, the highest corrosion resistance was detected for the coated sample. Cell viability measurements proved that osteosarcoma cells adhered to the surface of the coating, and the highest viability (90.5%) after one week of incubation was recorded for the (Zr,Ti)CN-coated sample.

Coatings of three compositions—TiN, TiON, and TiAlN—were compared in terms of the surface electrochemical corrosion in the simulated body fluid and cytotoxicity [114]. A number of experiments were carried out in order to study the mechanism of interaction between the blood platelets and samples with the proposed coatings in comparison with an uncoated sample of pure titanium. On the titanium control samples, the blood platelets were detected as aggregates, while on the coated samples, the blood platelets appeared as

singles, without any significant spread. In terms of corrosion resistance, the best result was demonstrated by the TiAlN coating. Cytotoxic studies testified that all the coatings under comparison passed the test, and therefore may be classified as non-cytotoxic materials.

A titanium oxide coating containing silver (Ag) nanoparticles was synthesized on a commercially pure titanium (CP–Ti) substrate by the method of reactive magnetron co-sputtering [115]. The results of the study testified to the presence of two factors affecting the inhibition of bacterial attachment to the surface of the samples: the surface morphology and the release of silver ions. The analysis results found the absence of cytotoxicity on fibroblast cells in all groups.

In [116], the study discussed the deposition of a coating of biocompatible calcium phosphate ($Ca_3(PO_4)_2$) on the surface of materials for biomedical implants by the method of rf-magnetron sputtering. Deposition parameters were investigated to obtain a coating in the form of stoichiometric crystalline hydroxyapatite or amorphous calcium phosphate at a Ca/P molar ratio from 1.53 to 3.88. The resulting coatings were homogeneous, dense, without pores, and without any defects or cracks. The ability to control the crystalline structure of the coating is of direct importance for the whole implant lifespan in living tissues. An amorphous coating will be absorbed faster than a crystalline one.

Coatings based on titanium carbide (TiC) have a wide range of biomedical applications due to their high hardness, low coefficient of friction, excellent corrosion resistance, and good biocompatibility [117]. To improve the properties of titanium carbide nanostructured coatings, they were deposited on a nickel–titanium substrate by the method of magnetron sputtering with preliminary plasma immersion ion implantation of a titanium sublayer. The study results prove that the Ti–TiC coating provided a significantly higher corrosion resistance and stability in comparison to an uncoated nickel–titanium substrate.

The experiments conducted to study potentiodynamic polarization in artificial saliva made it possible to evaluate the influence of deposition temperature on the microstructure and the corrosion resistance of ZrN coatings deposited through the DC reactive magnetron sputtering process on a Ti substrate [123]. It has been found that products with ZrN coatings deposited at relatively low temperatures have good corrosion resistance compared to uncoated products of titanium. At relatively high deposition temperatures, the corrosion resistance of samples to pitting increases due to the formation of oxides and oxynitrides of ZrN_xO_y and ZrO_2 on the surface of the ZrN coatings.

Despite the significant advantages of the above-described method, it also has considerable shortcomings. In particular, the adhesion to the substrate is noticeably lower in this case than that of the cathode vacuum-arc deposition method.

3.5. Modifying Coatings Deposited by the Vacuum-Arc Deposition Method

The vacuum-arc deposition (cathode-arc deposition) of coatings is a physical method of producing coatings in a vacuum by condensing them onto a substrate material from plasma flows generated on a target cathode in a cathode spot of a vacuum arc of a high-current low-voltage discharge propagating exclusively in vapors of the electrode material [124–127]. The method is used for the deposition of metal, ceramic, and composite coatings on various products. It is suitable for the deposition of coatings on substrates of low heat resistance (up to 200 °C). To improve the coating quality, appropriate equipment and technologies are used for filtering the phase of microparticles from a plasma flow, ion bombardment, and etching of the surface coating for its cleaning and thermal activation as well as ion implantation to increase the adhesion and modify the outer layer of the substrate [128–130].

Recently, the method of vacuum-arc deposition has become widespread due to the possibility of producing multilayer coatings of various architectures and compositions [131–133].

Delamination of coatings during implant insertion into human bones or during the implant lifespan is a serious problem, causing an ingress of toxic metals into the body tissues. In this regard, it is necessary to increase the adhesive bond strength between the coating and the substrate, which may be achieved by two additional operations:

(1) Preliminary (before coating deposition) mechanical processing of the substrate or processing by compression plasma flows in the surface melting mode;

(2) Finishing (after coating deposition) electromagnetic impulse action.

The first operation provides targeted regulation of the parameters of roughness and waviness of the substrate including in the range of values corresponding to the recommended parameters of medical implants [134]. The expansion of microroughness on the implant surface provides an increase in its area, and as a result, promotes implantability. An increase in roughness in the range of values provided by the action of compressive plasma flows also leads to an increase in the adhesion strength of the coating, both due to an increase in the surface area and a decrease in residual stresses in the coating being deposited [135]. A mathematical model was developed to describe the formation of a surface relief under the action of compression plasma flows [136]. In addition, it was found that plasma exposure led to a decrease in the concentration of elements toxic to the human body such as Al and V in the surface layer of the Ti–6Al–4V alloy [137].

Electromagnetic impulse action contributes to a decrease in the residual stresses in the coating and the "coating–substrate" transition layer. The conducted studies testify to the effectiveness of applying electromagnetic impulse action for both metal and nitride coatings [138,139].

Coatings from the nitrides of transition metals of Groups IV–VI of the D.I. Mendeleev's Periodic Table of Chemical Elements have been widely used in biomedical materials in the current decade.

The titanium nitride (TiN) coating used since the 1980s is still often applied in the manufacturing of endoprostheses [140–142] due to its good performance properties including high hardness (2400–2800 HV), good wear resistance, low coefficient of friction, increased wettability, and physiological inertness [142–144]. However, the corrosion resistance of a thin PVD coating of TiN is often unsatisfactory because of the coating defects (pores and cracks) that can form during the coating deposition. The above defects can create channels for an aggressive medium, up to contact with the substrate, thereby affecting the electrochemical behavior of the coatings [145]. The columnar microstructure of the TiN coating also weakens the protective function of the coatings and reduces their corrosion resistance [146]. An additional increase in the corrosion resistance is provided by the intermediate layer of Ti [147,148]. The presence of such an intermediate layer increases the corrosion resistance of the Ti-(Ti,Al)N coating in the solution of NaCl as well as in the media of H_2O and O_2 [149]. The corrosion resistance of the TiN coating also increases upon additional heat treatment in air [150]. Such an increase is associated with a decrease in the defectiveness of the coating due to the formation of the oxides of TiO_2 and Ti_2O_3 in the TiN structure. As a result, the volumetric expansion of the material takes place, and the coating structure becomes denser. In theory, thicker coatings provide higher corrosion resistance. However, too thick a coating may have lower corrosion resistance [151]. An increase in the thickness of the Ti–TiN coating leads to a growing number of internal defects, which allows oxygen to actively penetrate into the deep layers of the coating (for example, along the boundaries of microparticles embedded in the coating structure, while the length of the grain boundaries increases with a growth in the coating thickness). As a result of oxidation of the internal regions of the coating, its volumetric expansion takes place, and internal stresses increase. This process contributes to the formation of cracks, causing the damage of coatings and being, in turn, channels for the further penetration of oxygen [151].

Other two-component nitride coatings CrN [152–159], ZrN [160–167], and SiN [168–176], have also been applied for corrosion protection.

The CrN coating is highly resistant to corrosion in Ringer's and Hank's multi-component physiological solutions [152]. The intermediate Cr layer in the Cr–CrN coating, like the Ti layer in the Ti–TiN coating considered above, has a positive effect on the corrosion resistance [152]. The intermediate layer of pure metal significantly increases the adhesion between the coating and the substrate, which also has a positive effect on the corrosion resistance [153]. Furthermore, the corrosion resistance of titanium implants coated with

CrN can be increased by preliminary nitriding of the titanium substrate [154], as a result of which a transition layer is formed between the coating and the substrate containing the phases of ε-Ti_2N and δ-TiN, which improves the adhesion of the coating and, together with an increase in the tribological properties of the nitrided CrN-coated sample of Ti, improves the biocompatibility of the composite material.

It should be noted that in conditions of fatigue loading, the increased brittleness of the chromium nitride layers of the Cr–CrN multilayer coating led to a decrease in the fatigue life of the Ti–6Al–4V alloy [124]. The cracks formed in the coating propagated in a straight line through its layers, reaching the substrate and deepening further, thus violating the integrity of the surface of the titanium alloy.

The comparison of the properties of the CrN and TiN coatings proved that the CrN coating provided higher corrosion protection than the TiN coating in 3.5% NaCl solution and in 1 M H_2SO_4 solution [153] in the simulated body fluid (SBF) [154]. In addition, the coating of CrN outperformed the coatings of TiN, TiAlN, and a-C:H in terms of the tribological performance in the SBF [154].

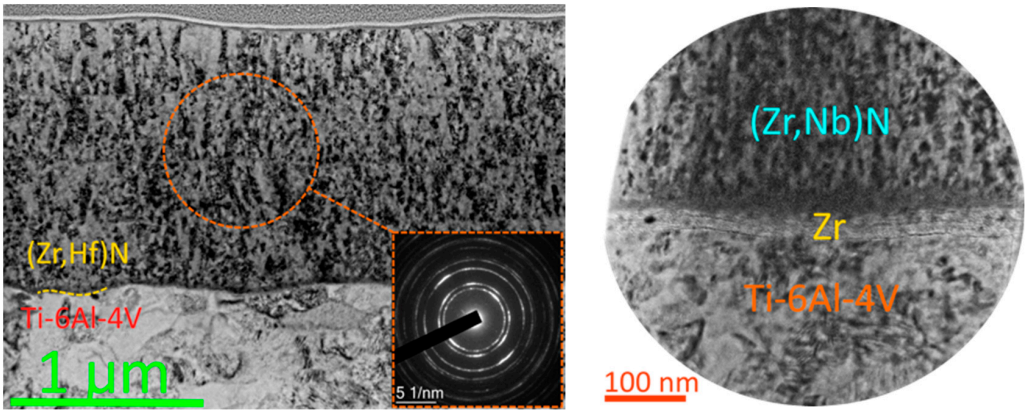
The coatings of Cr–CrN had a higher corrosion resistance in comparison with the coatings of Ti–TiN and Cr–TiN [155].

Another commercially used coating for implants is zirconium nitride (ZrN), which is mainly applied as a thin surface coating on endoprostheses. This coating is characterized by high mechanical and tribological properties combined with good biocompatibility [160,162].

The ZrN coating has a slightly lower microhardness compared to TiN. This coating is biocompatible and has antibacterial properties [163]. Therefore, the percentage of dead *S. oralis* bacteria was higher in the biofilms grown on TiN- and ZrN-coated disks of Ti than on uncoated disks and amounted to 51.84 ± 3.73 and 69.45 ± 1.15%, respectively, while the uncoated surfaces reduced the viability of *S. oralis* by only 6.4 ± 3.38% ($p < 0.001$) [163]. The highest fibroblast proliferation was detected on ZrN-coated disks compared to the uncoated samples and TiN-coated disks of Ti [163].

It is well-known that yttrium (Y) plays an important role in the phase transformation of zirconium dioxide, and appropriate treatment can result in the formation of a denser coating morphology, which is able to enhance the oxidation resistance. Thus, in [164], it was found that the ion implantation of yttrium into the surface of the ZrN coating promoted an increase in the oxidation resistance. At the same time, yttrium stabilized the tetragonal phase and prevented its transformation into monoclinic zirconium dioxide [164]. Such a mechanism of corrosion protection of the Y/ZrN coating deposited on a steel substrate as well as the possibilities of the PVD method, give reason to believe that such coatings may also be applied on titanium substrates.

In [165], the tribocorrosion behavior of the Zr/ZrN multilayer coatings in the simulated body fluid (SBF) was studied. The results proved that the Zr/ZrN multilayer coatings had higher corrosion and tribocorrosion resistance than the ZrN single-layer coating. The above was facilitated by effective inhibition of the penetration of a corrosive environment, both due to the formation of a passive film of ZrO_2, and due to the multilayer structure of the coating. In addition, the improved corrosion resistance of the ZrN coating and the suppression of crack propagation by the introduction of the Zr layer improved the tribological performance and corrosion protection. An additional effect on corrosion resistance can be obtained by introducing elements such as hafnium (Hf) and niobium (Nb) into the ZrN coating. Figure 7a shows the structure of the (Zr,Hf)N anti-corrosion coating, and Figure 7b shows the structure of the Zr-(Zr,Nb)N coating with a Zr adhesive sublayer deposited on a Ti–6Al–4V substrate.



(**a**) (**b**)

Figure 7. Structure of the (**a**) (Zr,Hf)N coating; (**b**) Zr-(Zr,Nb)N coating with Zr adhesive sublayer deposited on a Ti–6Al–4V substrate (TEM).

In recent years, much attention, both in scientific research and in industrial applications, has been paid to coatings of silicon nitride (SiN). These coatings are characterized by several useful properties: high thermal stability, chemical inertness, high hardness, and corrosion resistance. Due to the above-mentioned properties, the coatings of SiN may be effectively used as biocompatible and biomechanical coatings for biomedical devices and instruments. These coatings are used in the manufacturing of hip and knee joint implants as well as dental implants [172]. The use of SiN as a wear-resistant biocompatible coating on artificial joints made of Co–Cr–Mo alloys increases their durability [168–171]. Silicon nitride is a particularly promising material due to its ability to dissolve in biocompatible elements, while most other coatings exhibit very limited solubility, which is a problem in the formation of wear particles. At the same time, SiN has bacteriostatic properties [174–176].

The analysis of the available data suggests the following ranking of two-component nitrides from the best to worst in terms of corrosion resistance:

$$\mathrm{CrN} \rightarrow \mathrm{TiN} \rightarrow \mathrm{ZrN} \rightarrow \mathrm{SiN}.$$

It should be noted that this sequence is rather conditional, and requires further clarification.

Coatings produced from nitrides of zirconium, vanadium, titanium, and carbides of vanadium and chromium demonstrated the highest erosion resistance [177]. The corrosion resistance tests carried out in a tropical chamber proved that the coatings of ZrN, TiN, and TiC had the highest resistance to aggressive environments. The above results were also confirmed by the calculations of equilibrium potentials and the corresponding Pourbaix diagram. The coating of ZrN applied by the method of the filtered cathodic vacuum arc deposition (FCVAD) [178–183] had obvious advantages over the coating of ZrN deposited conventionally (by the arc-PVD method) [184].

Along with two-component nitride coatings, three- and multi-component coatings were also considered.

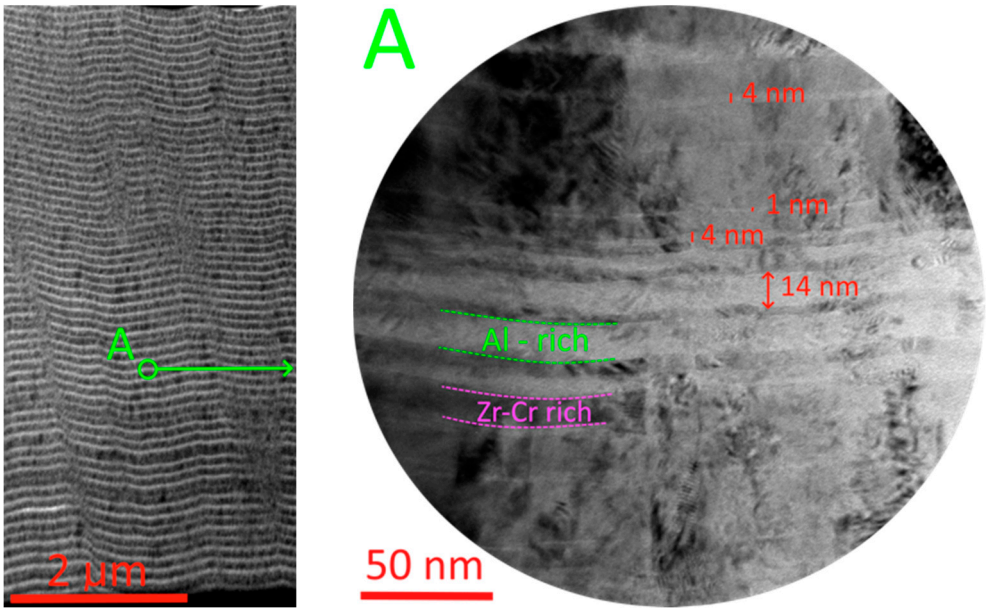
To modify the surfaces of hip and knee joint implants, three-component niobium and titanium nitride (Ti,Nb)N can be used. In comparison with TiN, the nitride of TiNbN has similar tribological properties, high resistance to wear and abrasive wear, and biocompatibility [185].

The (Ti,Si)N coating with a structure consisting of nanocrystalline TiN grains embedded in an amorphous Si_3N_4 matrix was deposited on samples of the Ti–6Al–4V alloy [186]. Compared to the uncoated sample, the (Ti,Si)N coating provided a significantly higher corrosion resistance.

The electrochemical properties of the nanostructured multilayer coating of Cr-(Ti,Al,Cr)N and single-layer coatings of (Ti,Al)N and CrN were considered in [187]. In comparison with the polarization curves of the uncoated samples and the (Ti,Al)N- and CrN-coated

samples, the corrosion potential of the multilayer coating of Cr-(Ti,Al,Cr)N shifted in the positive direction to −0.36 V, the corrosion current density decreased to 0.047 μAcm^{-2}, and the polarization resistance was 124.69 kΩ cm^2. The morphology of the Cr-(Ti,Al,Cr)N multilayer coating after the corrosion tests was close to the morphology of the coating after deposition. Therefore, the Cr-(Ti,Al,Cr)N multilayer coating exhibited excellent corrosion resistance compared to the uncoated samples and the samples with the (Ti,Al)N and CrN single-layer coatings. The authors explained the role of multilayer architecture in an increase in the corrosion resistance by the change in the initial growth regime of the coating, the blocking of pores, a decrease in the defectiveness of the coating structure, and, as a result, the formation of a dense coating with good corrosion resistance.

An example of a multilayer structure of a (Zr,Cr,Al)N coating that has a nanolayer structure with alternating nanolayers dominated by Zr–Cr or A, is shown in Figure 8.



(**a**) (**b**)

Figure 8. An example of a multilayer structure of a (Zr,Cr,Al)N coating that has a nanolayer structure with alternating nanolayers dominated by Zr–Cr or Al (TEM). (**a**) General coating structure; (**b**) nanolayer structure.

In [188,189], the coating of (Ti,Zr)N was also considered. According to the experimental results, this coating improved the corrosion resistance of the Ti samples by 200 times. The increased corrosion resistance may be explained by the nanocomposite structure of the TiN/ZrN layers with a dense columnar microstructure impervious to aggressive media. The multilayer structure of the coatings provokes the deflection of corrosion cracks along the layered surfaces and additionally slows down the dissolution of the coating [190].

To improve the osseointegration of titanium implants, hydrophilic coatings of (NbCuSi)N and (TiAlNb)N were developed [191]. The contact angle and biocompatibility of these coatings were studied using human umbilical cord mesenchymal stem cells (MSC). Although the multi-component coatings had a higher contact angle with the surface due to their uneven morphology, all samples had hydrophilic properties that favorably affected cell adhesion and proliferation.

In addition to nitride coatings, carbide coatings, in particular TiC, are also used to modify the surface of titanium implants. It has been found that a solid nanostructured layer of TiC protects a titanium implant from exposure to biological media, while simultaneously stimulating the adhesion, proliferation, and activity of osteoblasts, and also provides better contact between the implant and the bone in comparison with an uncoated implant of titanium [192].

Carbonitride coatings were also considered. A coating with a nanocomposite structure consisting of amorphous C, CNx, and nanocrystalline ZrCN was deposited onto samples of the Ti–6Al–4V titanium alloy [193]. The corrosion resistance of the ZrCN-coated samples was significantly higher than that of the uncoated samples of Ti–6Al–4V.

A Ti–CN coating deposited on a Ti–6Al–4V substrate was considered in [194]. Coatings of Ti–CN improve the overall reaction of the biomaterial, significantly increase wear resistance, and reduce the coefficient of friction.

The corrosion resistance of coatings is affected not only by their composition and structure, but also by the specific features of the deposition process. In particular, CAA-PVD (controlled accelerated arc) technology [195–197] can significantly reduce the disadvantages of the standard vacuum-arc processes associated with the formation of a microparticle phase, which significantly degrades the quality of products.

The tribocorrosion behavior of coated implants is significantly influenced by the adhesive bond strength between the coating and substrate (the greater the affinity of the substrate and coating materials, the higher the above adhesive bond strength). To improve the properties of coated titanium implants, it is advisable to form a diffusion sublayer that has a high affinity for both the coating and the substrate (for example, when a nitride coating is being produced, surface layers of the substrate are subjected to preliminary nitriding or the ion implantation of metal atoms that form the nitride phase of the coating is being carried out) [198–200].

The synthesis of nanostructured coatings uses a range of technological means, in particular:

- Bombardment (pulsed or continuous) of the deposited condensate with metal–gas ions with energies from 1–10 to 50–100 keV;
- Mixing of precipitated condensate particles under the influence of an assisting flow of high-energy gas–metal ions;
- Lowering the coating synthesis temperature, which leads to inhibition of the growth of its grains due to an increase in the degree of ionization of metal–gas ions of the condensed flow, thus forming nano-dispersed grain structures.

Another way to improve the properties of titanium implants is to make them antibacterial. In this case, it is preferable to apply coatings containing released metal ions [201] that have an antibacterial effect, rather than coatings containing antibiotics, which are associated with the risk of resistance to these antibiotics [202]. In particular, coatings with silver ions as well as ions of other metals (e.g., Cu^{+}, Zn^{+}, and Mg^{2+}) with antibacterial effect have become widely used.

In [203], the study examined the effect of a diamond-like carbon (DLC) coating with silver particles (DLC/Ag) obtained by pulsed dual-cathode (silver and graphite) filtered cathodic vacuum arc deposition (PDC-FCVA) on titanium substrates of Ti–Al6–V4. The tribological studies carried out on ultra-high-molecular-weight polyethylene (UHMWPE) beads in fetal bovine serum (BFS) found that the presence of silver in diamond-like carbon helped to reduce the wear of polymer surfaces. In addition, silver nanoparticles were critical for the antimicrobial effect.

To ensure better adhesion to the substrate during DLC coating deposition, an additional nitride layer is often used as well as a layer with a high silicon content (see Figure 9).

Ions of Zn^{+} and Cu^{+} contained in coatings also have excellent antibacterial properties due to their ability to penetrate and destroy bacterial cell membranes. Ions of Zn+ are also able to stimulate the proliferation and mineralization of osteocytes and promote calcium deposition in mesenchymal stem cells (MSCs) without causing cytotoxicity [204]. In addition, Zn is an essential microelement at several stages of bone formation, and it plays a positive role in enhancing the process of osseointegration [202].

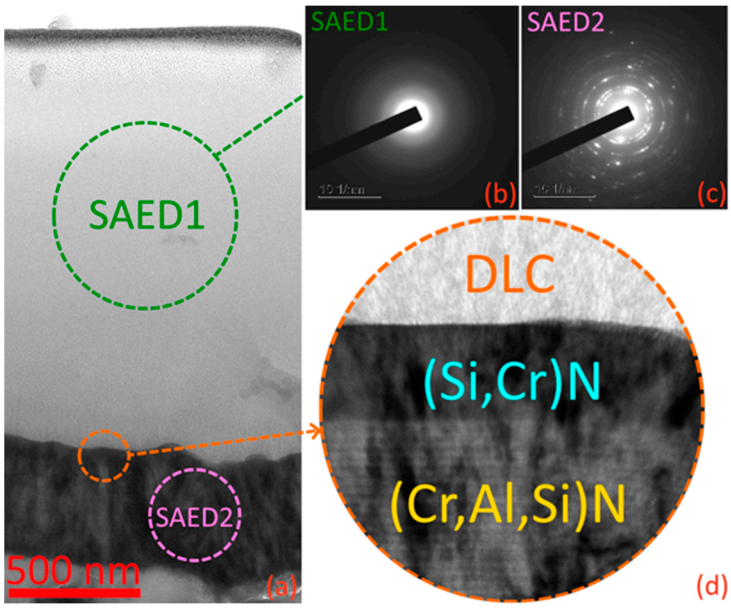


Figure 9. DLC coating with an adhesive sublayer (Cr,Al,Si)–(Si,Cr)N. (**a**) General structure of the coating layers; SAED (**b**) DLC layer and (**c**) adhesive sublayer (Cr,Al,Si)–(Si,Cr)N; (**d**) the structure of the adhesive sublayer (TEM).

Being an important microelement in the human body, Cu is harmless to the environment, while copper ions (Cu^{2+} and Cu^{+}) are able to adhere to the bacterial cell membrane, thus not only inhibiting the reproduction of various bacteria, but also effectively destroying some drug-resistant bacteria as well as destroying reactive oxygen species (ROS) that are generated by cells and interfere with their proteins and lipids [205]. In addition, Cu is able to promote the process of osteogenesis by increasing the expression of vascular endothelial growth factor (VEGF), and therefore, it has good prospects for use in coatings for orthopedic implants [202].

To further enhance the antibacterial effect, studies are underway to develop coatings based on the synergistic effect of various antibacterial metal ions as well as to introduce into the composition of such coatings bioactive particles that are able to enhance bone tissue regeneration (e.g., Ca^{+}). In [206], the comparison focused on the corrosion resistance, adhesion rate of proteins, in vitro cell proliferation, and the ability to inhibit bacteria of Cu–TiN coatings with two variants of implantable ions: Mg^{+} and Ca^{+}. The Cu–TiN coating with implanted ions of Mg^{+} had improved anti-corrosive properties, higher protein adsorption capacity, good cell proliferation and adhesion, and better antimicrobial properties.

4. Conclusions

The application of modifying coatings of various compositions deposited by various methods is an important condition for the effective use of medical implants designed for various purposes. The use of coatings solves a wide range of tasks at the same time. In particular, the coatings are applied in order to:

- Increase the biological inertness of an implant excluding complications associated with the phenomenon of metallosis;
- Increase the implant's ability to be integrated into the human body, contributing to the formation and strengthening of the appropriate biological environment on the implant surface;
- If necessary, and vice versa, reduce the implantability of a medical product (in cases of temporary implants, which should be later removed from the human body);
- Provide a limited antiseptic effect due to the formation of a thin surface layer with the inclusion of antiseptic substances;

Increase the wear resistance of implant elements subject to mechanical wear (for example, in a knee joint implant).

At the same time, the use of modifying coatings does not lead to a significant increase in the cost of an implant, and in some cases, it can even reduce its cost due to the use of less expensive substrate materials.

The methods of the coating deposition considered in this review have their advantages and disadvantages. In some cases, the best result may be achieved by combining different methods.

It can be concluded that it is promising to use the vacuum-arc deposition method to modify the surface of titanium implants in order to improve their biocompatibility and corrosion resistance as well as to impart additional bioactive functions (antibacterial, regenerative, etc.) by creating a multilayer nanostructured architecture of coatings of various compositions with increased adhesive bond strength in comparison to the coatings formed by other considered methods.

Coatings of various compositions and architectures, deposited using the PVD methods and technologies similar to them, are able to increase the corrosion resistance of products by several times or even orders of magnitude.

The generalization of the available research results proves that the most effective are coatings that meet the following conditions:

- Have a multilayer architecture including an adhesive (transition) layer that provides high adhesion to the substrate and a smooth transition of mechanical properties between the substrate and the corrosion-resistant layer as well as a corrosion-resistant layer itself, which, in turn, may have a multilayer structure.
- Have a multi-component composition that provides a high density and minimizes the number of internal defects in the coating, thus significantly increasing its anti-corrosive properties.
- Are characterized by additional bioactivity provided by coating layers containing releasable metal ions, while a synergistic mechanism between several ions can improve the antibacterial activity and cellular compatibility of an implant. For example, ions of calcium (Ca) and magnesium (Mg) can effectively promote osteoblast growth, and at the same time, ions of copper (Cu) and silver (Ag) have a significant antibacterial effect.

Author Contributions: Conceptualization, C.S. and A.V.; Methodology, C.S., A.V., V.U. and N.C.; Resources, S.G.; Data curation, C.S. and A.V.; Writing—original draft preparation, C.S. and A.V.; Writing—review and editing, S.G., C.S. and A.V.; Project administration, S.G.; Funding acquisition, S.G. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported financially by the Russian Science Foundation (project no. 23-49-10038) and the Belarusian Republican Foundation for Fundamental Research (#T23RNF-228).

Data Availability Statement: Not applicable.

Acknowledgments: The study used the equipment from the Center for Collective Use of Moscow State Technological University STANKIN (agreement no. 075-15-2021-695, 26/07/2021). The coating structure was investigated using the equipment at the Center for Collective Use of Scientific Equipment "Material Science and Metallurgy", purchased with the financial support of the Ministry of Science and Higher Education of the Russian Federation (GK 075-15-2021-696).

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Basova, T.V.; Vikulova, E.S.; Dorovskikh, S.I.; Hassan, A.; Morozova, N.B. The use of noble metal coatings and nanoparticles for the modification of medical implant materials. *Mater. Design* **2021**, *204*, 109672. [CrossRef]
2. Velu, R.; Calais, T.; Jayakumar, A.; Raspall, F. A comprehensive review on bio-nanomaterials for medical implants and feasibility studies on fabrication of such implants by additive manufacturing technique. *Materials* **2020**, *13*, 92. [CrossRef] [PubMed]
3. Chatterjee, S.; Saxena, M.; Padmanabhan, D.; Jayachandra, M.; Pandya, H.J. Futuristic medical implants using bioresorbable materials and devices. *Biosens. Bioelectron.* **2019**, *142*, 111489. [CrossRef] [PubMed]

4. Manam, N.S.; Harun, W.S.W.; Shri, D.N.A.; Ghani, S.A.C.; Kurniawan, T.; Ismail, M.H.; Ibrahim, M.H.I. Study of corrosion in biocompatible metals for implants: A review. *J. Alloys Compd.* **2017**, *701*, 698–715. [CrossRef]
5. Chen, Q.; Thouas, G.A. Metallic implant biomaterials. *Mat. Sci. Eng. R.* **2015**, *87*, 1–57. [CrossRef]
6. Kaur, M.; Singh, K. Review on titanium and titanium based alloys as biomaterials for orthopaedic applications. *Mat. Sci. Eng. C-Mater.* **2019**, *102*, 844–862. [CrossRef]
7. Sarraf, M.; Rezvani Ghomi, E.; Alipour, S.; Ramakrishna, S.; Liana Sukiman, N. A state-of-the-art review of the fabrication and characteristics of titanium and its alloys for biomedical applications. *Bio-Des. Manuf.* **2022**, *5*, 371–395. [CrossRef]
8. Annur, D.; Kartika, I.; Supriadi, S.; Suharno, B. Titanium and titanium based alloy prepared by spark plasma sintering method for biomedical implant applications—A review. *Mater. Res. Express* **2021**, *8*, 012001. [CrossRef]
9. Liu, X.; Chen, S.; Tsoi, J.K.H.; Matinlinna, J.P. Binary titanium alloys as dental implant materials—A review. *Regen. Biomater.* **2017**, *4*, 315–323. [CrossRef]
10. Cordeiro, J.M.; Barão, V.A.R. Is there scientific evidence favoring the substitution of commercially pure titanium with titanium alloys for the manufacture of dental implants? *Mat. Sci. Eng. C-Mater.* **2017**, *71*, 1201–1215. [CrossRef]
11. Blackert, E.; Bakkar, S.; Briseño-Murguia, S.; Kramer, M.; Barclay, J.; Carl, M.; Smith, J.; Young, M.L.; Aouadi, S.M. Textured TNZT surfaces via hydrothermal treatments for bone implant applications. *Thin Solid Film.* **2018**, *667*, 64–68. [CrossRef]
12. Jing, Z.; Zhang, T.; Xiu, P.; Cai, H.; Wei, Q.; Fan, D.; Lin, X.; Song, C.; Liu, Z. Functionalization of 3D-printed titanium alloy orthopedic implants: A literature review. *Biomed. Mater.* **2020**, *15*, 052003. [CrossRef] [PubMed]
13. Liang, S. Review of the design of titanium alloys with low elastic modulus as implant materials. *Adv. Eng. Mater.* **2020**, *22*, 2000555. [CrossRef]
14. Saghiri, M.-A.; Asatourian, A.; Garcia-Godoy, F.; Sheibani, N. The role of angiogenesis in implant dentistry part I: Review of titanium alloys, surface characteristics and treatments. *Med. Oral. Patol. Oral. Cir. Bucal* **2016**, *21*, e514–e525. [CrossRef]
15. Geetha, M.; Singh, A.K.; Asokamani, R.; Gogia, A.K. Ti based biomaterials, the ultimate choice for orthopaedic implants—A review. *Prog. Mater. Sci.* **2009**, *54*, 397–425. [CrossRef]
16. Zagorsky, V.A. Dental implantation. Materials and components. *Symb. Sci.* **2016**, *9*, 132–136.
17. Mishra, S.K.; Chowdhary, R. Evolution of dental implants through the work of per-ingvar branemark: A systematic review. *Indian. J. Dent. Res.* **2020**, *31*, 930–956.
18. Sidelnikov, A.I. Comparative characteristics of materials of the titanium group used in the production of modern dental implants. *Infodent Int.* **2000**, *5*, 10–12.
19. *ISO 5832-2:2018*; Implants for Surgery—Metallic Materials—Part 2: Unalloyed Titanium. ISO: Geneva, Switzerland, 2018. Available online: https://www.iso.org/standard/69907.html (accessed on 14 January 2023).
20. *ASTM F67-13(2017)*; Standard Specification for Unalloyed Titanium, for Surgical Implant Applications (UNS R50250, UNS R50400, UNS R50550, UNS R50700). ASTM: West Conshohocken, PA, USA, 2017. Available online: https://www.astm.org/standards/f67 (accessed on 14 January 2023).
21. Hua, F.; Mon, K.; Pasupathi, P.; Gordon, G.; Shoesmith, D. A review of corrosion of titanium grade 7 and other titanium alloys in nuclear waste repository environments. *Corrosion* **2005**, *61*, 987–1003. [CrossRef]
22. Bolzoni, L.; Yang, F. Development of Cu-bearing powder metallurgy Ti alloys for biomedical applications. *J. Mech. Behav. Biomed. Mater.* **2019**, *97*, 41–48. [CrossRef]
23. Gibson, L.J.; Ashby, M.F. Cancellous bone. In *Cellular Solids: Structure and Properties*, 2nd ed.; Cambridge University Press: Cambridge, UK, 1997; pp. 429–452.
24. Sumner, D.R.; Galante, J.O. Determinants of stress shielding: Design versus materials versus interface. *Clin. Orthop. Relat. Res.* **1992**, *274*, 202–212. [CrossRef]
25. Huiskes, R.; Weinans, H.; Vanrietbergen, B. The relationship between stress shielding and bone resorption around total hip stems and the effects of flexible materials. *Clin. Orthop. Relat. Res.* **1992**, *274*, 124–134. [CrossRef]
26. Hongbo, L.J.Z. Development of β-type medical titanium alloys' performance. *J. Oral. Sci. Res.* **2020**, 501–508.
27. Ozan, S.; Lin, J.; Li, Y.; Zhang, Y.; Munir, K.; Jiang, H.; Wen, C. Deformation mechanism and mechanical properties of a thermomechanically processed β Ti–28Nb–35.4Zr alloy. *J. Mech. Behav. Biomed. Mater.* **2018**, *78*, 224–234. [CrossRef]
28. Plaine, A.H.; da Silva, M.R.; Bolfarini, C. Effect of thermo-mechanical treatments on the microstructure and mechanical properties of the metastable 2-type Ti-35Nb-7Zr-5Ta alloy. *Mater. Res.* **2019**, *22*, e20180462. [CrossRef]
29. Bai, Y.; Hao, Y.L.; Li, S.J.; Hao, Y.Q.; Yang, R.; Prima, F. Corrosion behavior of biomedical Ti-24Nb-4Zr-8Sn alloy in different simulated body solutions. *Mater. Sci. Eng. C-Mater. Biol. Appl.* **2013**, *33*, 2159–2167. [CrossRef]
30. Li, X.; Ye, S.L.; Yuan, X.N.; Yu, P. Fabrication of biomedical Ti-24Nb-4Zr-8Sn alloy with high strength and low elastic modulus by powder metallurgy. *J. Alloys Compd.* **2019**, *772*, 968–977. [CrossRef]
31. Ho, W.F.; Ju, C.P.; Chern Lin, J.H. Structure and properties of cast binary Ti-Mo alloys. *Biomaterials* **1999**, *20*, 2115–2122. [CrossRef]
32. Oliveira, N.T.C.; Guastaldi, A.C. Electrochemical stability and corrosion resistance of Ti-Mo alloys for biomedical applications. *Acta Biomater.* **2009**, *5*, 399–405. [CrossRef]
33. Attar, H.; Ehtemam-Haghighi, S.; Kent, D.; Dargusch, M.S. Laser additive manufacturing of low-cost Ti–Mo alloys: Microstructural evolution, phase analysis, and mechanical properties. *Adv. Eng. Mater.* **2023**, *25*, 2201265. [CrossRef]

34. Luo, R.D.; Yuan, Y.X.; Ren, J.K.; Li, F.; Yang, Y.J.; He, Z.Y.; Jiang, Y.H. Novel function-structure-integrated Ti-Mo-Cu alloy combined with excellent antibacterial properties and mechanical compatibility as implant application. *J. Alloys Compd.* **2023**, *945*, 169323. [CrossRef]
35. Cai, B.; Lei, K.; Sun, C.; Li, G.; Guo, Z. Surface modification of new innocuous Ti–Mo–Zr based alloys for biomedical applications. *BioMetals* **2022**, *35*, 1271–1280. [CrossRef] [PubMed]
36. Musadaq, Y.M.; Naji, G.A.-H.; Jamal Al-Deen, H.H.J. Effect of yttrium addition on mechanical and physical properties of Ti15Mo alloy as an implant materia. *J. Med. Chem. Sci.* **2023**, *6*, 986–999.
37. Xin, X.; Yu, H.; Lv, H.; Ren, J.; Yu, W.; Ding, X.; Zhou, Y.; Zhao, J. Developing a New Beta-Type of Ti–Si/Sn Alloys for Targeted Orthopedic Therapeutics: Assessments of Biological Characteristics. *Adv. Eng. Mater.* **2021**, *23*, 2000430. [CrossRef]
38. Jarfors, A.E.W.; Butler, D.L.; Goi, K.L.S. Microstructure formation of porous sintered Ti–Si–Zr compacts with mechanically alloyed-activated Ti–Si and TiH_2 powders. *J. Alloys Compd.* **2014**, *594*, 202–210. [CrossRef]
39. Goldenberg, Y.; Tee, J.W.; Salinas-La Rosa, C.M.; Murphy, M. Spinal metallosis: A systematic review. *Eur. Spine J.* **2016**, *25*, 1467–1473. [CrossRef]
40. Ho, J.; Mahajan, J.; Taylor, M.; Byers, A.; Arauz, P.; Kwon, Y.-M. Metallosis in cemented titanium alloy total knee arthroplasty without apparent metal-on-metal articulation. *Knee* **2018**, *25*, 728–731. [CrossRef]
41. Sahan, I.; Anagnostakos, K. Metallosis after knee replacement: A review. *Arch. Orthop. Traum Su* **2020**, *140*, 1791–1808. [CrossRef]
42. Wolf, M.B. Comprehensive diagnosis of whole-body acid–base and fluid-electrolyte disorders using a mathematical model and whole-body base excess. *J. Clin. Monit. Comput.* **2015**, *29*, 475–490. [CrossRef]
43. Karlov, A.V.; Shakhov, V.P. *External Fixation Systems and Regulatory Mechanisms of Optimal Biomechanics*; STT: Tomsk, Russia, 2001; p. 480. ISBN 5-93629-093-X.
44. Steinemann, S.G.; Perren, S.M. Titanium alloys as metallic biomaterials. In Proceedings of the Fifth World Conference on Titanium, Congress-Center, Munich, Germany, 10–14 September 1984; Volume 2, pp. 1327–1334.
45. Albrektsson, T.; Hansson, H.A.; Ivarsson, B. Interface analysis of titanium and zirconium bone implants. *Biomaterials* **1985**, *6*, 97–101. [CrossRef]
46. Eshmatov, A.R. Analysis of purulent-inflammatory complications of surgical treatment of skeletal fractures of technological origin. *Bull. Kyrg. State Med. Acad. Named After I.K. Akhunbayev* **2016**, *1*, 111–114.
47. Sampiev, M.T.; Laka, A.A.; Agzamov, D.S.; Balashov, S.P.; Makinyan, L.G.; Shevchenko, A.A.; Karimov, R.F.; Ramlugon, K. Metallosis caused by sliding titanium structures in patients with scoliosis. *Vestn. Russ. Sci. Cent. Roentgenoradiol. Minist. Healthc. Russ. Fed.* **2015**, *15*, 5.
48. Rozhnova, O.M.; Prokhorenko, V.M.; Sadovoy, M.A.; Samokhin, A.G.; Ageeva, T.A. Pathogenetic factors in the formation of aseptic instability of joint endoprostheses (literature review). *Sib. Sci. Med. J.* **2015**, *35*, 84–89.
49. Zavilgelsky, G.B.; Kotova, V.Y.; Khrulnova, S.A.; Manukhov, I.V. Evaluation of the toxic effect of nanomaterials on living organisms. *Biotechnology* **2013**, *6*, 8–17.
50. Razina, I.S.; Chernova, V.I.; Kolokolov, M.A.; Musin, I.N. Evaluation of the diffusion of implant elements for osteosynthesis during their operation. *Her. Technol. Univ.* **2014**, *17*, 162–166.
51. Steinemann, S.G. Metal implants and surface reactions. *Injury* **1996**, *27* (Suppl. 3), S/C16–S/C22. [CrossRef] [PubMed]
52. Shamsutdinov, I.I.; Bayazitova, L.T.; Grebenshchikova, M.M.; Mironov, M.M. Antimicrobial properties of nanostructured plasma condensates. *Her. Technol. Univ.* **2017**, *20*, 149–151.
53. Rod Fixation of Long Bones—Errors and Complications. Available online: http://www.mosmedclinic.ru/conf_library/2003/15/880 (accessed on 1 February 2023).
54. Principles of Treatment of Bone Fractures. Part 2—Indications for the Removal of Metal Retainers. Available online: http://voenobr.ru/uchmaterial/travma/192-princippereloma.html (accessed on 1 February 2023).
55. Ilizarov, G.A. The value of the complex of optimal mechanical and biological factors in the regenerative process in transosseous osteosynthesis. In Proceedings of the Abstracts of the All-Union Symposium with The Participation of Foreign Specialists, Kurgan, Russia, 20–22 September 1983; pp. 5–15.
56. Osteosynthesis. *A Guide for Doctors*; Tkachenko, S.S., Ed.; Meditsina: Leningrad, Russia, 1987.
57. Ude, C.C.; Esdaille, C.J.; Ogueri, K.S.; Kan, H.-M.; Laurencin, S.J.; Nair, L.S.; Laurencin, C.T. The mechanism of metallosis after total hip arthroplasty. *Regen. Eng. Transl. Med.* **2021**, *7*, 247–261. [CrossRef]
58. Bottle, A.; Parikh, S.; Aylin, P.; Loeffler, M. Risk factors for early revision after total hip and knee arthroplasty: National observational study from a surgeon and population perspective. *PLoS ONE* **2019**, *14*, e0214855. [CrossRef]
59. Singh, J.A.; Yu, S.; Chen, L.; Cleveland, J.D. Rates of total joint replacement in the United States: Future Projections to 2020-2040 Using the National Inpatient Sample. *J. Rheumatol.* **2019**, *46*, 1134–1140. [CrossRef]
60. Es'Kin, N.A.; Andreeva, T.M. *Trauma Cases, Orthopadic Morbidity, State of Trauma and Orthopaedic Assistance Service for Population of Russian Federation in 2020*; CITO: Moscow, Russia, 2022.
61. Sheng, X.; Wang, A.; Wang, Z.; Liu, H.; Wang, J.; Li, C. Advanced surface modification for 3D-printed titanium alloy implant interface functionalization. *Front. Bioeng. Biotechnol.* **2022**, *10*, 850110. [CrossRef] [PubMed]
62. Mironov, M.M.; Grebenshchikova, M.M.; Starodumova, E.V. Study of metal ion migration from protective nano-structured coatings for implants. *Her. Technol. Univ.* **2016**, *19*, 23–26.

63. Shesterikov, E.V. Methods and Equipment for the Formation of Hybrid Biologically Compatible Coatings on Implants for Surgery. Ph.D. Thesis, Tomsk Polytechnic University, Tomsk, Russia, 2012.
64. Izmailov, R.R. Biomimetic Synthesis, Structure, Physico-Chemical Properties of Carbonate Hydroxylapatite. Ph.D. Thesis, NNSTU, Nizhny Novgorod, Russia, 2016.
65. Yushchenko, K.A.; Borisov, Y.S.; Voinarovich, S.G.; Kislitsa, A.N.; Kuzmich-Yanchuk, E.K. Two-layer biocermet coating titanium—hydroxyapatite. *Autom. Weld.* **2011**, *12*, 46–49.
66. Shishatskaya, E.I. Biocompatible and functional properties of the hybrid composite polyhydroxybutyrate/hydroxyapatite. *Russ. J. Transpl. Artif. Organs* **2006**, *3*, 34–38.
67. Kobayashi, M.; Abdulmajeed, A.A.; Moon, J.; Shahramian, K.; Punkkinen, R.; Shimada, J.; Vallittu, P.K.; Lassila, L.V. The effect of ultraviolet treatment on TiO2 nanotubes: A study of surface characteristics, bacterial adhesion, and gingival fibroblast response. *Metals* **2022**, *12*, 80. [CrossRef]
68. Jin, M.; Zhu, J.; Meng, Z.; Jiang, X.; Chen, Z.; Xu, J.; Gao, H.; Zhu, J.; Wu, F. TiO_2 nanotubes-MoS_2/PDA-LL-37 exhibits efficient anti-bacterial activity and facilitates new bone formation under near-infrared laser irradiation. *Biomed. Mater.* **2022**, *17*, 045025. [CrossRef]
69. Pan, C.; Liu, T.; Yang, Y.; Liu, T.; Gong, Z.; Wei, Y.; Quan, L.; Yang, Z.; Liu, S. Incorporation of Sr^{2+} and Ag nanoparticles into TiO_2 nanotubes to synergistically enhance osteogenic and antibacterial activities for bone repair. *Mater. Design* **2020**, *196*, 109086. [CrossRef]
70. Qiao, H.; Zhang, C.; Dang, X.; Yang, H.; Wang, Y.; Chen, Y.; Ma, L.; Han, S.; Lin, H.; Zhang, X.; et al. Gallium loading into a polydopamine-functionalised $SrTiO_3$ nanotube with combined osteoinductive and antimicrobial activities. *Ceram. Int.* **2019**, *45*, 22183–22195. [CrossRef]
71. Xia, H.; Wang, D.; Tian, A.; Xu, Y.; Gong, H.; Li, Z.; Miao, J. Near-Infrared-Activated MoS_2(S)–Ag_3PO_4 Coating for Rapid Bacteria-Killing. *Coatings* **2022**, *12*, 1263. [CrossRef]
72. Ma, Y.; Yan, J.; Yan, T.; Wang, Q.; Bao, Z. Biological properties of Cu-bearing and Ag-bearing titanium-based alloys and their surface modifications: A review of antibacterial aspect. *Front. Mater.* **2022**, *96*, 999794. [CrossRef]
73. Fang, J.; Wan, Y.; Sun, Y.; Qi, M.; Cheng, S.; Li, C.; Zhou, Y.; Xu, L.; Dong, B.; Wang, L. Near-infrared-activated nanohybrid coating with black phosphorus/zinc oxide for efficient biofilm eradication against implant-associated infections. *Chem. Eng. J.* **2022**, *435*, 134935. [CrossRef]
74. Shaygani, H.; Seifi, S.; Shamloo, A.; Golizadeh, M.; Rahnamaee, S.Y.; Alishiri, M.; Ebrahimi, S. Novel bilayer coating on gentamicin-loaded titanium nanotube for orthopedic implants applications. *Int. J. Pharm.* **2023**, *636*, 122764. [CrossRef] [PubMed]
75. Radin, S.; Ducheyne, P. Controlled release of vancomycin from thin sol–gel films on titanium alloy fracture plate material. *Biomaterials* **2007**, *28*, 1721–1729. [CrossRef] [PubMed]
76. Andrade del Olmo, J.; Pérez-Álvarez, L.; Sáez Martínez, V.; Benito Cid, S.; Ruiz-Rubio, L.; Pérez González, R.; Vilas-Vilela, J.L.; Alonso, J.M. Multifunctional antibacterial chitosan-based hydrogel coatings on Ti6Al4V biomaterial for biomedical implant applications. *Int. J. Biol. Macromol.* **2023**, *231*, 123328. [CrossRef]
77. Vereschaka, A. Improvement of working efficiency of cutting tools by modifying its surface properties by application of wear-resistant complexes. *Adv. Mat. Res.* **2013**, *712-715*, 347–351. [CrossRef]
78. Kuzin, V.V.; Grigor'ev, S.N.; Volosova, M.A. Effect of a TiC coating on the stress-strain state of a plate of a high-density nitride ceramic under nonsteady thermoelastic conditions. *Refract. Ind. Ceram.* **2014**, *54*, 376–380. [CrossRef]
79. Vereschaka, A.A.; Volosova, M.A.; Grigoriev, S.N.; Vereschaka, A.S. Development of wear-resistant complex for high-speed steel tool when using process of combined cathodic vacuum arc deposition. *Procedia CIRP* **2013**, *9*, 8–12. [CrossRef]
80. Volosova, M.; Grigoriev, S.; Metel, A.; Shein, A. The role of thin-film vacuum-plasma coatings and their influence on the efficiency of ceramic cutting inserts. *Coatings* **2018**, *8*, 287. [CrossRef]
81. Fominski, V.Y.; Grigoriev, S.N.; Celis, J.P.; Romanov, R.I.; Oshurko, V.B. Structure and mechanical properties of W-Se-C/diamond-like carbon and W-Se/diamond-like carbon bi-layer coatings prepared by pulsed laser deposition. *Thin Solid Film.* **2012**, *520*, 6476–6483. [CrossRef]
82. Vereschaka, A.; Tabakov, V.; Grigoriev, S.; Aksenenko, A.; Sitnikov, N.; Oganyan, G.; Seleznev, A.; Shevchenko, S. Effect of adhesion and the wear-resistant layer thickness ratio on mechanical and performance properties of ZrN-(Zr,Al,Si)N coatings. *Surf. Coat. Technol.* **2019**, *357*, 218–234. [CrossRef]
83. Vereschaka, A.; Grigoriev, S.; Tabakov, V.; Migranov, M.; Sitnikov, N.; Milovich, F.; Andreev, N. Influence of the Nanostructure of Ti-TiN-(Ti,Al,Cr)N Multilayer Composite Coating on Tribological Properties and Cutting Tool Life. *Tribol. Int.* **2020**, *150*, 106388. [CrossRef]
84. Grigoriev, S.; Vereschaka, A.; Milovich, F.; Tabakov, V.; Sitnikov, N.; Andreev, N.; Sviridova, T.; Bublikov, J. Investigation of multicomponent nanolayer coatings based on nitrides of Cr, Mo, Zr, Nb, and Al. *Surf. Coat. Technol.* **2020**, *401*, 126258. [CrossRef]
85. Asri, R.I.M.; Harun, W.S.W.; Hassan, M.A.; Ghani, S.A.C.; Buyong, Z. A review of hydroxyapatite-based coating techniques: Sol-gel and electrochemical depositions on biocompatible metals. *J. Mech. Behav. Biomed. Mater.* **2016**, *57*, 95–108. [CrossRef] [PubMed]
86. Weng, W.; Zhuang, J.; Lin, S.; Dong, L.; Cheng, K. Recent development of electrochemical deposition of biologically functionalized coatings. *Kuei Suan Jen Hsueh Pao/J. Chin. Ceram. Soc.* **2017**, *45*, 1539–1547.

87. Li, T.-T.; Ling, L.; Lin, M.-C.; Peng, H.-K.; Ren, H.-T.; Lou, C.-W.; Lin, J.-H. Recent advances in multifunctional hydroxyapatite coating by electrochemical deposition. *J. Mater. Sci.* **2020**, *55*, 6352–6374. [CrossRef]
88. Kulakov, A.A.; Kasparov, A.S.; Porfenchuk, D.A. Factors affecting osseointegration and the use of early functional loading to reduce the treatment time for dental implantation. *Stomatologiya* **2019**, *4*, 107–115.
89. Esposito, M.; Ardebili, Y.; Worthington, H.V. Interventions for replacing missing teeth: Different types of dental implants. *Cochrane Database Syst. Rev.* **2014**, *7*, CD003815. [CrossRef]
90. Sharma, A.; McQuillan, A.J.; Shibata, Y.; Sharma, L.A.; Waddell, J.N.; Duncan, W.J. Histomorphometric and histologic evaluation of titanium-zirconium (aTiZr) implants with anodized surfaces. *J. Mater. Sci. Mater. Med.* **2016**, *27*, 86. [CrossRef]
91. Sawase, T.; Jimbo, R.; Wennerberg, A.; Suketa, N.; Tanaka, Y.; Atsuta, M. A novel characteristic of porous titanium oxide implants. *Clin. Oral. Implants Res.* **2007**, *18*, 680–685. [CrossRef]
92. Caous, J.S.; Lövenklev, M.; Fäldt, J.; Langton, M. Adhesion of Streptococcus mitis and Actinomyces oris in co-culture to machined and anodized titanium surfaces as affected by atmosphere and pH. *BMC Oral. Health* **2013**, *13*, 4. [CrossRef]
93. Shubladze, G.K. Comparison of implant anodized surface advantage with other types of surfaces. *Med. Alph.* **2014**, *3*, 20–25.
94. Apachitei, I.; Leoni, A.; Riemslag, A.C.; Fratila-Apachitei, L.E.; Duszczyk, J. Enhanced fatigue performance of porous coated Ti6Al4V biomedical alloy. *Appl. Surf. Sci.* **2011**, *257*, 6941–6944. [CrossRef]
95. Hu, H.; Qiao, Y.; Meng, F.; Liu, X.; Ding, C. Enhanced apatite-forming ability and cytocompatibility of porous and nanostructured $TiO_2/CaSiO_3$ coating on titanium. *Colloid. Surface B.* **2013**, *101*, 83–90. [CrossRef] [PubMed]
96. Valanezhad, A.; Tsuru, K.; Maruta, M.; Kawachi, G.; Matsuya, S.; Ishikawa, K. A new biocompatible coating layer applied on titanium substrates using a modified zinc phosphatizing method. *Surf. Coat. Technol.* **2012**, *206*, 2207–2212. [CrossRef]
97. Chouirfa, H.; Bouloussa, H.; Migonney, V.; Falentin-Daudré, C. Review of titanium surface modification techniques and coatings for antibacterial applications. *Acta Biomater.* **2019**, *83*, 37–54. [CrossRef]
98. Andrina, K.; Finšgar, K.M. A review of techniques for the application of bioactive coatings on metal-based implants to achieve controlled release of active ingredients. *Mater. Design* **2022**, *27*, 110653.
99. Wang, D.; Bierwagen, G.P. Sol-gel coatings on metals for corrosion protection. *Prog. Org. Coat.* **2009**, *64*, 327–338. [CrossRef]
100. Tranquillo, E.; Bollino, F. Surface modifications for implants lifetime extension: An overview of sol-gel coatings. *Coatings* **2020**, *10*, 589. [CrossRef]
101. Wu, L.-K.; Wu, J.-J.; Wu, W.-Y.; Cao, F.-H.; Jiang, M.-Y. Sol–gel-based coatings for oxidation protection of TiAl alloys. *J. Mater. Sci.* **2020**, *55*, 6330–6351. [CrossRef]
102. Zheng, C.Y.; Nie, F.L.; Zheng, Y.F.; Cheng, Y.; Wei, S.C.; Ruan, L.; Valiev, R.Z. Enhanced corrosion resistance and cellular behavior of ultrafine-grained biomedical NiTi alloy with a novel $SrO\text{-}SiO_2\text{-}TiO_2$ sol-gel coating. *Appl. Surf. Sci.* **2011**, *257*, 5913–5918. [CrossRef]
103. Mohammad, N.F.; Ahmad, R.N.; Mohd Rosli, N.L.; Abdul Manan, M.S.; Marzuki, M.; Wahi, A. Sol gel deposited hydroxyapatite-based coating technique on porous titanium niobium for biomedical applications: A mini review. *Mater. Today-Proc.* **2021**, *41*, 127–135. [CrossRef]
104. Liu, S.-H.; Trelles, J.P.; Li, C.-J.; Li, C.-X.; Guo, H.-B. A review and progress of multiphase flows in atmospheric and low pressure plasma spray advanced coating. *Mater. Today Phys.* **2022**, *27*, 100832. [CrossRef]
105. Kumar, H.; Bhaduri, G.A.; Manikandan, S.G.K.; Kamaraj, M.; Shiva, S. Microstructural Characterization and Tribological Properties of Atmospheric Plasma Sprayed High Entropy Alloy Coatings. *J. Therm. Spray. Techn* **2022**, *31*, 1956–1974. [CrossRef]
106. Xu, J.L.; Joguet, D.; Cizek, J.; Khor, K.A.; Liao, H.L.; Coddet, C.; Chen, W.N. Synthesis and characterization on atomphospheric plasma sprayed amorphous silica doped hydrxoyapatite coatings. *Surf. Coat. Technol.* **2012**, *206*, 4659–4665. [CrossRef]
107. Altomare, L.; Bellucci, D.; Bolelli, G.; Bonferroni, B.; Cannillo, V.; De Nardo, L.; Gadow, R.; Killinger, A.; Lusvarghi, L.; Sola, A.; et al. Microstructure and in vitro behaviour of 45S5 bioglass coatings deposited by high velocity suspension flame spraying (HVSFS). *J. Mater. Sci: Mater. Med.* **2011**, *22*, 1303–1319. [CrossRef] [PubMed]
108. Novikov, S.V.; Tamazov, I.D.; Matveev, A.I.; Topoljanskij, P.A.; Topoljanskij, A.P. Optimization of the surface of titanium dental implants of grade 5 alloy by barrier glass ceramic coating. *Clin. Dent.* **2021**, *24*, 29–36. [CrossRef]
109. Sun, H.; Zhang, Y.; Dou, L.; Song, X.; Sun, C. Surface modification of pure titanium to improve its anti-inflammatory function. *Eur. J. Inflamm.* **2015**, *13*, 204–208. [CrossRef]
110. Zhou, X.; Siman, R.; Lu, L.; Mohanty, P. Argon atmospheric plasma sprayed hydroxyapatite/Ti composite coating for biomedical applications. *Surf. Coat. Technol.* **2012**, *207*, 343–349. [CrossRef]
111. Baltatu, M.S.; Vizureanu, P.; Sandu, A.V.; Munteanu, C.; Istrate, B. microstructural analysis and tribological behavior of Ti-based alloys with a ceramic layer using the thermal spray method. *Coatings* **2020**, *10*, 1216. [CrossRef]
112. Chang, Y.-Y.; Lai, C.-H.; Hsu, J.-T.; Tang, C.-H.; Liao, W.-C.; Huang, H.-L. Antibacterial properties and human gingival fibroblast cell compatibility of TiO_2/Ag compound coatings and ZnO films on titanium-based material. *Clin. Oral. Investig.* **2012**, *16*, 95–100. [CrossRef]
113. Braic, V.; Braic, M.; Balaceanu, M.; Vladescu, A.; Zoita, C.N.; Titorencu, I.; Jinga, V. (Zr,Ti)CN coatings as potential candidates for biomedical applications. *Surf. Coat. Technol.* **2011**, *206*, 604–609. [CrossRef]
114. Subramanian, B.; Muraleedharan, C.V.; Ananthakumar, R.; Jayachandran, M. A comparative study of titanium nitride (TiN), titanium oxy nitride (TiON) and titanium aluminum nitride (TiAlN), as surface coatings for bio implants. *Surf. Coat. Technol.* **2011**, *205*, 5014–5020. [CrossRef]

115. Song, D.-H.; Uhm, S.-H.; Kim, S.-E.; Kwon, J.-S.; Han, J.-G.; Kim, K.-N. Synthesis of titanium oxide thin films containing antibacterial silver nanoparticles by a reactive magnetron co-sputtering system for application in biomedical implants. *Mater. Res. Bull.* **2012**, *47*, 2994–2998. [CrossRef]
116. Surmenev, R.A.; Surmeneva, M.A.; Evdokimov, K.E.; Pichugin, V.; Peitsch, T.; Epple, M. The influence of the deposition parameters on the properties of an rf-magnetron-deposited nanostructured calcium phosphate coating and a possible growth mechanism. *Surf. Coat. Technol.* **2011**, *205*, 3600–3606. [CrossRef]
117. Shanaghi, A.; Chu, P.K.; Rouhaghdam, A.R.S.; Xu, R.; Hu, T. Structure and corrosion resistance of Ti/TiC coatings fabricated by plasma immersion ion implantation and deposition on nickel-titanium. *Surf. Coat. Technol.* **2012**, *229*, 151–155. [CrossRef]
118. Lex, J.; Koucheki, R.; Stavropoulos, N.; DiMichele, J.; Toor, J.; Tsoi, K.; Ferguson, P.; Turcotte, R.; Papagelopoulos, P. Mega-prosthesis anti-bacterial coatings: A comprehensive translational review. *Acta Biomater.* **2022**, *140*, 136–148. [CrossRef]
119. Baigonakova, G.A.; Marchenko, E.S.; Yasenchuk, Y.F.; Kokorev, O.V.; Vorozhtsov, A.B.; Kulbakin, D.E. Microstructural characterization, wettability and cytocompatibility of gradient coatings synthesized by gas nitriding of three-layer Ti/Ni/Ti nanolaminates magnetron sputtered on the TiNi substrate. *Surf. Coat. Technol.* **2022**, *436*, 128291. [CrossRef]
120. Larhlimi, H.; Ghailane, A.; Makha, M.; Alami, J. Magnetron sputtered titanium carbide-based coatings: A review of science and technology. *Vacuum* **2022**, *197*, 110853. [CrossRef]
121. Anwar, U.-H. Synthesis, microstructural characterization and nanoindentation of Zr, Zr-nitride and Zr-carbonitride coatings deposited using magnetron sputtering. *J. Adv. Res.* **2021**, *29*, 107–119.
122. Montazerian, M.; Hosseinzadeh, F.; Migneco, C.; Fook, M.V.L.; Baino, F. Bioceramic coatings on metallic implants: An overview. *Ceram. Int.* **2022**, *48*, 8987–9005. [CrossRef]
123. Roman, D.; Bernardi, J.; de Amorim, C.L.; de Souza, F.S.; Spinelli, A.; Giacomelli, C.; Figueroa, C.A.; Baumvol, I.J.; Basso, R.L. Effect of deposition temperature on microstructure and corrosion resistance of ZrN thin films deposited by DC reactive magnetron sputtering. *Mater. Chem. Phys.* **2011**, *130*, 147–153. [CrossRef]
124. Metel, A.S.; Grigoriev, S.N.; Melnik, Y.A.; Prudnikov, V.V. Glow discharge with electrostatic confinement of electrons in a chamber bombarded by fast electrons. *Plasma Phys. Rep.* **2011**, *37*, 628–637. [CrossRef]
125. Grigoriev, S.N.; Melnik, Y.A.; Metel, A.S.; Panin, V.V.; Prudnikov, V.V. A compact vapor source of conductive target material sputtered by 3-keV ions at 0.05-Pa pressure. *Instrum. Exp. Tech.* **2009**, *52*, 731. [CrossRef]
126. Grigoriev, S.; Volosova, M.; Fyodorov, S.; Lyakhovetskiy, M.; Seleznev, A. DLC-coating application to improve the durability of ceramic tools. *J. Mater. Eng. Perform.* **2019**, *28*, 4415–4426. [CrossRef]
127. Sobol', O.V.; Andreev, A.A.; Grigoriev, S.N.; Gorban', V.F.; Volosova, M.A.; Aleshin, S.V.; Stolbovoi, V.A. Effect of high-voltage pulses on the structure and properties of titanium nitride vacuum-arc coatings. *Met. Sci. Heat. Treat.* **2012**, *54*, 195–203. [CrossRef]
128. Sobol', O.V.; Andreev, A.A.; Grigoriev, S.N.; Gorban', V.F.; Volosova, M.A.; Aleshin, S.V.; Stolbovoy, V.A. Physical characteristics, structure and stress state of vacuum-arc TiN coating, deposition on the substrate when applying high-voltage pulse during the deposition. *Probl. Atom. Sci. Tech.* **2011**, *4*, 174–177.
129. Vereschaka, A.; Tabakov, V.; Grigoriev, S.; Sitnikov, N.; Milovich, F.; Andreev, N.; Bublikov, J. Investigation of wear mechanisms for the rake face of a cutting tool with a multilayer composite nanostructured Cr–CrN-(Ti,Cr,Al,Si)N coating in high-speed steel turning. *Wear* **2019**, *438–439*, 203069. [CrossRef]
130. Vereschaka, A.A.; Vereschaka, A.S.; Grigoriev, S.N.; Kirillov, A.K.; Khaustova, O. Development and research of environmentally friendly dry technological machining system with compensation of physical function of cutting fluids. *Procedia CIRP* **2013**, *7*, 311–316. [CrossRef]
131. Grigoriev, S.N.; Volosova, M.A.; Fedorov, S.V.; Okunkova, A.A.; Pivkin, P.M.; Peretyagin, P.Y.; Ershov, A. Development of DLC-Coated Solid SiAlON/TiN Ceramic End Mills for Nickel Alloy Machining: Problems and Prospects. *Coatings* **2021**, *11*, 532. [CrossRef]
132. Grigoriev, S.; Vereschaka, A.; Milovich, F.; Sitnikov, N.; Andreev, N.; Bublikov, J.; Kutina, N. Investigation of the properties of the Cr,Mo-(Cr,Mo,Zr,Nb)N-(Cr,Mo,Zr,Nb,Al)N multilayer composite multicomponent coating with nanostructured wear-resistant layer. *Wear* **2021**, *468–469*, 203597. [CrossRef]
133. Vereschaka, A.; Tabakov, V.; Grigoriev, S.; Sitnikov, N.; Oganyan, G.; Andreev, N.; Milovich, F. Investigation of wear dynamics for cutting tools with multilayer composite nanostructured coatings in turning constructional steel. *Wear* **2019**, *420–421*, 17–37. [CrossRef]
134. Laskovnev, A.P.; Cherenda, N.N.; Basalai, A.V.; Uglov, V.V.; Isobello, A.Y.; Danilchik, I.K.; Shimansky, V.I.; Astashinsky, V.M. Method for Obtaining Implants. Eurasian Patent 029487, 30 April 2018.
135. Leyvi, A.Y.; Yalovets, A.P. Interaction of concentrated energy flows with matter. Numerical experiment. Interaction of Radiation with Solids. In Proceedings of the 12th International Conference, Minsk, Belarus, 19–22 September 2017; Uglov, V.V., Ed.; pp. 337–339.
136. Astashinsky, V.M.; Leyvi, A.Y.; Yalovets, A.P.; Uglov, V.V.; Cherenda, N.N. Formation of relief on a metallic target surface under the action of compression plasma flows. *J. Surf. Investig-X-Ra* **2014**, *8*, 519–523. [CrossRef]
137. Cherenda, N.N.; Basalai, A.V.; Shymanski, V.I.; Uglov, V.V.; Astashynski, V.M.; Kuzmitski, A.M.; Laskovnev, A.P.; Remnev, G.E. Modification of Ti-6Al-4V alloy element and phase composition by compression plasma flows impact. *Surf. Coat. Technol.* **2018**, *355C*, 148–154. [CrossRef]

138. Seydametov, S.V.; Loskutov, S.V. Influence of pulsed electromagnetic processing on structural rearrangements of titanium alloy VT3-1. *J. Phys. Surf. Eng.* **2016**, *1*, 4–8.
139. Anisovich, A.G.; Bisyuk, L.V.; Gologan, V.F.; Bologa, M.K.; Bobanova, Z.I.; Ivashku, S.K.; Azharonok, V.V.; Krat'ko, L.E. Effect of a high-frequency electromagnetic field on the properties of chromium coatings. *Surf. Eng. Appl. Electrochem.* **2013**, *49*, 101–106. [CrossRef]
140. Gotman, I.; Gutmanas, E.Y.; Hunter, G. 1.8 Wear-Resistant Ceramic Films and Coatings. In *Comprehensive Biomaterials II*, 2nd ed.; Ducheyne, P., Ed.; Elsevier Ltd.: Amsterdam, The Netherlands, 2017; Volume 1, pp. 165–203.
141. Coll, B.F.; Jacquot, P. Surface modification of medical implants and surgical devices using TiN layers. *Surf. Coat. Technol.* **1988**, *36*, 867–878. [CrossRef]
142. Scarano, A.; Piattelli, M.; Vrespa, G.; Caputi, S.; Piattelli, A. Bacterial adhesion on titanium nitride-coated and uncoated implants: An in vivo human study. *J. Oral. Implantol.* **2003**, *29*, 80–85. [CrossRef]
143. Ducheyne, P.; Healy, K.E.; Grainger, D.W.; Hutmacher, D.W.; Kirkpatrick, C.J. *Comprehensive Biomaterials*; Ducheyne, P., Ed.; Elsevier Ltd.: Amsterdam, The Netherlands, 2011.
144. Van Hove, R.P.; Sierevelt, I.N.; Van Royen, B.J.; Nolte, P.A. Titanium-nitride coating of orthopaedic implants: A review of the literature. *BioMed Res. Int.* **2015**, 485975. [CrossRef]
145. Grips, V.K.W.; Selvi, V.E.; Barshilia, H.C.; Rajam, K.S. Effect of electroless nickel interlayer on the electrochemical behavior of single layer CrN, TiN, TiAlN coatings and nanolayered TiAlN/CrN multilayer coatings prepared by reactive dc magnetron sputtering. *Electrochim. Acta* **2006**, *51*, 3461–3468. [CrossRef]
146. Liu, C.; Bi, Q.; Matthews, A. EIS comparison on corrosion performance of PVD TiN and CrN coated mild steel in 0.5 N NaCl aqueous solution. *Corros. Sci.* **2001**, *43*, 1953–1961. [CrossRef]
147. Vega, J.; Scheerer, H.; Andersohn, G.; Oechsner, M. Experimental studies of the effect of Ti interlayers on the corrosion resistance of TiN PVD coatings by using electrochemical methods. *Corros. Sci.* **2018**, *133*, 240–250. [CrossRef]
148. Zhou, D.P.; Peng, H.; Zhu, L.; Guo, H.B.; Gong, S.K. Microstructure, hardness and corrosion behaviour of TiN/Ti multilayer coatings produced by plasma activated EB-PVD. *Surf. Coat. Technol.* **2014**, *258*, 102–107. [CrossRef]
149. Zhang, M.M.; Xin, L.; Ding, X.Y.; Zhu, S.L.; Wang, F.H. Effects Ti/TiAlN composite multilayer coatings on corrosion resistance of titanium alloy in solid NaCl-H2O-O2 at 600 °C. *J. Alloys Compd.* **2017**, *734*, 307–317. [CrossRef]
150. Li, R.; Wang, S.; Zhou, D.; Pu, J.; Yu, M.; Guo, W. A new insight into the NaCl-induced hot corrosion mechanism of TiN coatings at 500 °C. *Corros. Sci.* **2020**, *174*, 108794. [CrossRef]
151. Zhang, M.; Niu, Y.; Xin, L.; Su, J.; Li, Y.; Wu, T.; Zhao, H.; Zhang, Y.; Xie, W.; Zhu, S.; et al. Studies on corrosion resistance of thick Ti/TiN multilayer coatings under solid NaCl–H2O–O2 at 450 °C. *Ceram. Int.* **2020**, *46*, 19274–19284. [CrossRef]
152. Gilewicz, A.; Chmielewska, P.; Murzynski, D.; Dobruchowska, E.; Warcholinski, B. Corrosion resistance of CrN and CrCN/CrN coatings deposited using cathodic arc evaporation in Ringer's and Hank's solutions. *Surf. Coat. Technol.* **2016**, *299*, 7–14. [CrossRef]
153. Li, T.; Liu, T.; Wei, H.; Hussain, S.; Wang, J.; Zeng, W.; Peng, X.; Wang, Z. First-principles calculations of the twin boundary energies and adhesion energies of interfaces for cubic face-centered transition-metal nitrides and carbides. *Appl. Surf. Sci.* **2015**, *355*, 1132–1135. [CrossRef]
154. Fernandes, M.F.; Velloso, V.M.O.; Voorwald, H.J.C. Cr/CrN multilayer coating effect on the surface integrity of Ti-6Al-4V alloy under fatigue loadings. *Procedia CIRP* **2022**, *108*, 746–751. [CrossRef]
155. Chim, Y.C.; Ding, X.Z.; Zeng, X.T.; Zhang, S. Oxidation resistance of TiN, CrN, TiAlN and CrAlN coatings deposited by lateral rotating cathode arc. *Thin Solid Film.* **2009**, *517*, 4845–4849. [CrossRef]
156. Nam, N.D.; Kim, M.J.; Jo, D.S.; Kim, J.G.; Yoon, D.H. Corrosion protection of Ti/TiN, Cr/TiN, Ti/CrN, and Cr/CrN multi-coatings in simulated proton exchange membrane fuel cell environment. *Thin Solid Film.* **2013**, *545*, 380–384. [CrossRef]
157. Çelik, İ. Influence of CrN Coating on Electrochemical Behavior of Plasma Nitrided Pure Titanium in Bio-simulated Environment. *J. Bionic Eng.* **2016**, *13*, 150–155. [CrossRef]
158. Geyao, L.; Yang, D.; Wanglin, C.; Chengyong, W. Development and application of physical vapor deposited coatings for medical devices: A review. *Procedia CIRP* **2020**, *89*, 250–262. [CrossRef]
159. Wang, Q.; Zhou, F.; Wang, C.; Yuen, M.-F.; Wang, M.; Qian, T.; Matsumoto, M.; Yan, J. Comparison of tribological and electrochemical properties of TiN, CrN, TiAlN and a-C:H coatings in simulated body fluid. *Mater. Chem. Phys.* **2015**, *158*, 74–81. [CrossRef]
160. Herbster, M.; Döring, J.; Nohava, J.; Lohmann, C.H.; Halle, T.; Bertrand, J. Retrieval study of commercially available knee implant coatings TiN, TiNbN and ZrN on TiAl6V4 and CoCr28Mo6. *J. Mech. Behav. Biomed.* **2020**, *112*, 104034. [CrossRef]
161. Skjöldebrand, C.; Tipper, J.L.; Hatto, P.; Bryant, M.; Hall, R.M.; Persson, C. Current status and future potential of wear-resistant coatings and articulating surfaces for hip and knee implants. *Mater. Today Bio.* **2022**, *15*, 100270. [CrossRef]
162. B Braun, AS Advanced Surface. Coating Technology—7 Layers to Protect You, (n.d.). Available online: https://www.bbraun.com/en/products/b0/as-advanced-surface.html%0A (accessed on 27 February 2023).
163. Brunello, G.; Brun, P.; Gardin, C.; Ferroni, L.; Bressan, E.; Meneghello, R.; Zavan, B.; Sivolella, S. Biocompatibility and antibacterial properties of zirconium nitride coating on titanium abutments: An in vitro study. *PLoS ONE* **2018**, *13*, e0199591. [CrossRef]
164. Zhou, Q.G.; Bai, X.D.; Xue, X.Y.; Ling, Y.H.; Chen, X.W.; Xu, J.; Wang, D.R. The influence of Y ion implantation on the oxidation behaviour of ZrN coating. *Vacuum* **2004**, *76*, 517–521. [CrossRef]

165. Cai, F.; Zhou, Q.; Chen, J.; Zhang, S. Effect of inserting the Zr layers on the tribo-corrosion behavior of Zr/ZrN multilayer coatings on titanium alloys. *Corros. Sci.* **2023**, *213*, 111002. [CrossRef]
166. Hajduga, M.B.; Bobinski, R. TiN, ZrN and DLC nanocoatings—a comparison of the effects on animals, in-vivo study. *Mat. Sci. Eng. C.* **2019**, *104*, 109949. [CrossRef]
167. Floroian, L.; Craciun, D.; Socol, G.; Dorcioman, G.; Socol, M.; Badea, M.; Craciun, V. Titanium implants' surface functionalization by pulsed laser deposition of TiN, ZrC and ZrN hard films. *Appl. Surf. Sci.* **2017**, *417*, 175–182. [CrossRef]
168. Filho, L.; Schmidt, S.; Leifer, K.; Engqvist, H.; Högberg, H.; Persson, C. Towards Functional Silicon Nitride Coatings for Joint Replacements. *Coatings* **2019**, *9*, 73. [CrossRef]
169. Pettersson, M.; Tkachenko, S.; Schmidt, S.; Berlind, T.; Jacobson, S.; Hultman, L.; Engqvist, H.; Persson, C. Mechanical and tribological behavior of silicon nitride and silicon carbon nitride coatings for total joint replacements. *J. Mech. Behav. Biomed.* **2013**, *25*, 41–47. [CrossRef]
170. Skjöldebrand, C.; Schmidt, S.; Vuong, V.; Pettersson, M.; Grandfield, K.; Högberg, H.; Engqvist, H.; Persson, C. Influence of substrate heating and nitrogen flow on the composition, morphological and mechanical properties of SiNx coatings aimed for joint replacements. *Materials* **2017**, *10*, 173. [CrossRef] [PubMed]
171. Shi, Z.; Wang, Y.; Du, C.; Huang, N.; Wang, L.; Ning, C. Silicon nitride films for the protective functional coating: Blood compatibility and biomechanical property study. *J. Mech. Behav. Biomed.* **2012**, *16*, 9–20. [CrossRef] [PubMed]
172. Raza, S.M.; Khurshid, Z.; Zafar, M.S.; Najeeb, S.; Yaqin, S.A.U. 15—Silicon nitride (SiN): An emerging material for dental implant applications. In *Dental Implants: Materials, Coatings, Surface Modifications and Interfaces with Oral Tissues*; Zafar, M.S., Khurshid, Z., Khan, A.S., Najeeb, S., Sefat, F., Eds.; Woodhead Publishing Series in Biomaterials: England, UK, 2020; pp. 287–299.
173. Filho, L.C.; Schmidt, S.; Goyenola, C.; Skjöldebrand, C.; Engqvist, H.; Högberg, H.; Toble, M.; Persson, C. The effect of N, C, Cr, and Nb content on silicon nitride coatings for joint applications. *Materials* **2020**, *13*, 1896. [CrossRef] [PubMed]
174. Filho, L.C.; Schmidt, S.; López, A.; Cogrel, M.; Leifer, K.; Engqvist, H.; Högberg, H.; Persson, C. The effect of coating density on functional properties of SiNx coated implants. *Materials* **2019**, *12*, 3370. [CrossRef] [PubMed]
175. Webster, T.J.; Patel, A.A.; Rahaman, M.N.; Bal, B.S. Anti-infective and osteointegration properties of silicon nitride, poly (ether ether ketone), and titanium implants. *Acta Biomater.* **2012**, *8*, 4447–4454. [CrossRef] [PubMed]
176. Das, M.; Bhimani, K.; Balla, V.K. In vitro tribological and biocompatibility evaluation of sintered silicon nitride. *Mater. Lett.* **2018**, *212*, 130–133. [CrossRef]
177. Muboyadzhyan, S.A. Erosion-resistant metal nitride coatings and carbide and their plasmochemical synthesis. *Russ. J. Gen. Chem.* **2011**, *81*, 1053–1060. [CrossRef]
178. Vereschaka, A.; Oganyan, M.; Bublikov, Y.; Sitnikov, N.; Deev, K.; Pupchin, V.; Mokritskii, B. Increase in Efficiency of End Milling of Titanium Alloys Due to Tools with Multilayered Composite Nano-Structured Zr-ZrN-(Zr,Al)N and Zr-ZrN-(Zr,Cr,Al)N Coatings. *Coatings* **2018**, *8*, 395. [CrossRef]
179. Vereschaka, A.; Tabakov, V.; Grigoriev, S.; Sitnikov, N.; Milovich, F.; Andreev, N.; Sotova, C.; Kutina, N. Investigation of the influence of the thickness of nanolayers in wear-resistant layers of Ti-TiN-(Ti,Cr,Al)N coating on destruction in the cutting and wear of carbide cutting tools. *Surf. Coat. Technol.* **2020**, *385*, 125402. [CrossRef]
180. Grigoriev, S.N.; Vereschaka, A.A.; Fyodorov, S.V.; Sitnikov, N.N.; Batako, A.D. Comparative analysis of cutting properties and nature of wear of carbide cutting tools with multi-layered nano-structured and gradient coatings produced by using of various deposition methods. *Int. J. Adv. Manuf. Technol.* **2017**, *90*, 3421–3435. [CrossRef]
181. Grigoriev, S.; Vereschaka, A.; Uglov, V.; Milovich, F.; Cherenda, N.; Andreev, N.; Migranov, M.; Seleznev, A. Influence of tribological properties of Zr-ZrN-(Zr,Cr,Al)N and Zr-ZrN-(Zr,Mo,Al)N multilayer nanostructured coatings on the cutting properties of coated tools during dry turning of Inconel 718 alloy. *Wear* **2023**, *512–513*, 204521. [CrossRef]
182. Grigoriev, S.; Vereschaka, A.; Milovich, F.; Tabakov, V.; Sitnikov, N.; Andreev, N.; Bublikov, J.; Sotova, C. Investigation of the properties of Ti-TiN-(Ti,Al,Nb,Zr)N composite coating and its efficiency in increasing wear resistance of metal cutting tools. *Surf. Coat. Technol.* **2021**, *421*, 127432. [CrossRef]
183. Vereschaka, A.; Milovich, F.; Migranov, M.; Andreev, N.; Alexandrov, I.; Muranov, A.; Mikhailov, M.; Tatarkanov, A. Investigation of the tribological and operational properties of (Me_x,Mo_y,$Al_{1-(x+y)}$)N (Me–Ti, Zr or Cr) coatings. *Tribol. Int.* **2022**, *165*, 107305. [CrossRef]
184. Vereshchaka, A.A. Multilayer Composite Coating. Russian Federation Patent 2198243, 10 February 2003.
185. Serro, A.P.; Completo, C.; Colaço, R.; dos Santos, F.; da Silva, C.L.; Cabral, J.M.S.; Araújo, H.; Pires, E.; Saramago, B. A comparative study of titanium nitrides, TiN, TiNbN and TiCN, as coatings for biomedical applications. *Surf. Coat. Technol.* **2009**, *203*, 3701–3707. [CrossRef]
186. Peng, S.; Xu, J.; Li, Z.; Jiang, S.; Munroe, P.; Xie, Z.H.; Lu, H. A reactive-sputter-deposited TiSiN nanocomposite coating for the protection of metallic bipolar plates in proton exchange membrane fuel cells. *Ceram. Int.* **2020**, *46*, 2743–2757. [CrossRef]
187. Wang, L.; Wang, M.; Chen, H. Corrosion mechanism investigation of TiAlN/CrN superlattice coating by multi-arc ion plating in 3.5 wt% NaCl solution. *Surf. Coat. Technol.* **2020**, *391*, 125660. [CrossRef]
188. Vereschaka, A.; Grigoriev, S.; Sitnikov, N.; Milovich, F.; Aksenenko, A.; Andreev, N. Investigation of performance and cutting properties of carbide tool with nanostructured multilayer Zr-ZrN-($Zr_{0.5}$,$Cr_{0.3}$,$Al_{0.2}$)N coating. *Int. J. Adv. Manuf. Technol.* **2019**, *102*, 2953–2965. [CrossRef]

189. Lin, M.T.; Wan, C.H.; Wu, W. Comparison of corrosion behaviors between SS304 and Ti substrate coated with (Ti,Zr)N thin films as Metal bipolar plate for unitized regenerative fuel cell. *Thin Solid Film.* **2013**, *544*, 162–169. [CrossRef]
190. Vereschaka, A.A.; Grigoriev, S.N. Study of cracking mechanisms in multi-layered composite nano-structured coatings. *Wear* **2017**, *378-379*, 43–57. [CrossRef]
191. Kravchenko, Y.O.; Garkush, I.E.; Taran, A.V.; Coy, E.; Iatsunskyi, I.; Diedkova, K.; Roshchupkin, A.; Tymoshenko, O.; Pogorielov, M.; Misiruk, I. Development of hydrophilic NbCuSi(N) &TiAlNb(N) coatings as a new strategy for medical implants modification. *Ceram. Int.* **2023**, *49*, 4099–4108.
192. Veronesi, F.; Giavaresi, G.; Fini, M.; Longo, G.; Ioannidu, C.A.; Scotto d'Abusco, A.; Superti, F.; Panzini, G.; Misiano, C.; Palattella, A.; et al. Osseointegration is improved by coating titanium implants with a nanostructured thin film with titanium carbide and titanium oxides clustered around graphitic carbon. *Mat. Sci. Eng. C* **2017**, *70*, 264–271. [CrossRef] [PubMed]
193. Xu, J.; Huang, H.J.; Li, Z.; Xu, S.; Tao, H.; Munroe, P.; Xie, Z.-H. Corrosion behavior of a ZrCN coated Ti alloy with potential application as a bipolar plate for proton exchange membrane fuel cell. *J. Alloys Compd.* **2016**, *663*, 718–730. [CrossRef]
194. De Viteri, V.S.; Barandika, M.G.; De Gopegui, U.R.; Bayón, R.; Zubizarreta, C.; Fernández, X.; Igartua, A.; Agullo-Rueda, F. Characterization of Ti-C-N coatings deposited on Ti6Al4V for biomedical applications. *J. Inorg. Biochem.* **2012**, *117*, 359–366. [CrossRef]
195. Grigoriev, S.; Vereschaka, A.; Zelenkov, V.; Sitnikov, N.; Bublikov, J.; Milovich, F.; Andreev, N.; Mustafaev, E. Specific features of the structure and properties of arc-PVD coatings depending on the spatial arrangement of the sample in the chamber. *Vacuum* **2022**, *200*, 111047. [CrossRef]
196. Grigoriev, S.; Vereschaka, A.; Zelenkov, V.; Sitnikov, N.; Bublikov, J.; Milovich, F.; Andreev, N.; Sotova, C. Investigation of the influence of the features of the deposition process on the structural features of microparticles in PVD coatings. *Vacuum* **2022**, *202*, 111144. [CrossRef]
197. Grigoriev, S.; Vereschaka, A.; Milovich, F.; Andreev, N.; Bublikov, J.; Seleznev, A.; Kutina, N. Influence of Mo content on the properties of multilayer nanostructured coatings based on the (Mo,Cr,Al)N system. *Tribol. Int.* **2022**, *174*, 107741. [CrossRef]
198. Grigoriev, S.; Vereschaka, A.; Milovich, F.; Migranov, M.; Andreev, N.; Bublikov, J.; Sitnikov, N.; Oganyan, G. Investigation of the tribological properties of Ti-TiN-(Ti,Al,Nb,Zr)N composite coating and its efficiency in increasing wear resistance of metal cutting tools. *Tribol. Int.* **2021**, *164*, 107236. [CrossRef]
199. Grigoriev, S.; Vereschaka, A.; Uglov, V.; Milovich, F.; Tabakov, V.; Cherenda, N.; Andreev, N.; Migranov, M. Influence of the tribological properties of the Zr,Hf-(Zr,Hf)N-(Zr,Me,Hf,Al)N coatings (where Me is Mo, Ti, or Cr) with a nanostructured wear-resistant layer on their wear pattern during turning of steel. *Wear* **2023**, *518-519*, 204624. [CrossRef]
200. Vereschaka, A.; Milovich, F.; Andreev, N.; Seleznev, A.; Alexandrov, I.; Muranov, A.; Mikhailov, M.; Tatarkanov, A. Comparison of properties of ZrHf-(Zr,Hf)N-(Zr,Hf,Cr,Mo,Al)N and Ti-TiN-(Ti,Cr,Al)N nanostructured multilayer coatings and cutting properties of tools with these coatings during turning of nickel alloy. *J. Manuf. Process.* **2023**, *88*, 184–201. [CrossRef]
201. Dubadi, R.; Huang, S.D.; Jaroniec, M. Mechanochemical synthesis of nanoparticles for potential antimicrobial applications. *Materials* **2023**, *16*, 1460. [CrossRef] [PubMed]
202. Chen, X.; Zhou, J.; Qian, Y.; Zhao, L.Z. Antibacterial coatings on orthopedic implants. *Mater. Today Bio.* **2023**, *19*, 100586. [CrossRef] [PubMed]
203. Endrino, J.L.; Sánchez-López, J.C.; Galindo, R.E.; Horwat, D.; Anders, A. Beneficial silver: Antibacterial nanocomposite Ag-DLC coating to reduce osteolysis of orthopaedic implants. *J. Phys. Conf. Ser.* **2010**, *252*, 012005. [CrossRef]
204. de Araujo Bastos Santana, L.; Oliveira Junior, P.H.; Damia, C.; dos Santos Tavares, D.; dos Santos, E.A. Bioactivity in SBF versus trace element effects: The isolated role of Mg^{2+} and Zn^{2+} in osteoblast behavior. *Mater. Sci. Eng. C* **2021**, *118*, 11132. [CrossRef] [PubMed]
205. Jacobs, A.; Renaudin, G.; Forestier, C.; Nedelec, J.-M.; Descamps, S. Biological properties of copper-doped biomaterials for orthopedic applications: A review of antibacterial, angiogenic and osteogenic aspects. *Acta Biomater.* **2020**, *117*, 21–39. [CrossRef]
206. Liu, C.; Zhao, M.; Song, X.; Li, D. The comparative biological properties of Mg^{+} or Ca^{+} implanted Cu–TiN nanocomposite coatings on titanium alloys. *Vacuum* **2021**, *194*, 110618. [CrossRef]