

Bioactive coatings of metallic orthopedic implants: functional properties and clinical potential

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Abstract. Use of metallic orthopedic implants (screws, plates, intramedullary rods) has several problems, such as inadequate biological integration and high infection risk. This review summarizes current insights on functional coatings for metallic orthopedic implants concerning their osteoinductive, osteoconductive, immunomodulatory, and antimicrobial properties and evaluating their clinical application potential. Key bioactive coatings include hydroxyapatite and bioactive glass, alongside with nanostructured and ion-doped layers. The deposition techniques, namely plasma spraying, sol-gel technology, anodization, electrophoretic deposition, and gas-detonation spraying, are analyzed. It is ascertained that the hydroxyapatite and bioactive glass coatings substantially enhance biocompatibility and osseointegration. Ion doping (strontium, zinc, magnesium) further boosts osteoinductive properties, while nanostructuring enhances cell adhesion and minimizes inflammatory responses. Antimicrobial coatings with silver, antibiotics, and bactericidal agents significantly reduce infectious complications. Among coating deposition methods, plasma spraying, sol-gel processes, and gas-detonation spraying show notable industrial applicability. Multifunctional and "smart" coatings demonstrate strong clinical efficiency and promise widespread adoption. Advancements in coating technology and optimization of material compositions will decrease complications and enhance treatment outcomes for patients with bone injuries and defects.

Keywords: bioactive coatings, orthopedic implants, deposition methods, biological integration, infection risk.

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1. Introduction

Orthopedic implants made of metal alloys (screws, plates, intramedullary rods) have been widely used for stabilization of fractures and substitution of bone defects. However, their use encounters two main issues, namely, insufficient biological integration, which may cause instability of fixation, and the risk of infection complications. The periodicity of infections after the osteosynthesis of long bones is equal to 1–4%, while it can reach 30% in cases of high-severity open fractures [1]. Decrease in the periodicity of infections and improvement of the osseointegration are the critical conditions for successful functioning of implants.

In this context, a promising method to provide positive osteoconductive and antimicrobial effects is

coating of implants with bioactive materials. Particularly, application of hydroxyapatite (HA), bioglasses, doped oxides, and nanostructured layers has become the subject of active investigations over the last decade [2]. Today, the attention of researchers is being paid to improvement and optimization of the bioactive coating deposition methods, namely, plasma spraying, electrophoretic deposition, sol-gel technology, anodizing, and gas-detonation spraying. These methods allow creation of multilayer composite bioactive coatings of complex structures with smart functional properties [3–5].

Another important direction of investigations is tuning of physical and chemical properties of the coatings being formed according to the specific clinical cases: osteoporosis, open fractures, multifractional injuries, or infected defects.

In this review, we carry out systematization and critical analysis of the data from modern references concerning the properties of bioactive and antimicrobial coatings of metallic implants, evaluating the efficiency of various materials, deposition methods, prospects for clinical applications, and the key directions of future investigations.

2. Methodology

The reference search was carried out using the scientometric databases PubMed, Scopus, and Web of Science using the following keywords: orthopedic implants, bioactive coatings, hydroxyapatite, bioactive glass, antimicrobial surface, silver coating, gentamicin-releasing implants, *etc.* The period was from 2019 to 2024. We analyzed both experimental and clinical investigations concerning the functional properties of coatings for metallic implants, including biocompatibility, osseointegration, and antimicrobial activity of the coatings. We did not analyze the studies without initial data or published in a language different from English. The total number of the analyzed articles was 184. With account of importance of the discussed information, 40 of them were included in the reference list.

3. Results and discussion

3.1. Interaction of coatings with bone cells

Biocompatibility is the ability of a material to function normally in an organism without causing toxic reaction or immune response. It means that adhesion of osteogenic cells should occur on the surface of the orthopedic implant, with subsequent formation of a new bone. The basic materials, namely, titanium and inox steel, are inert and do not facilitate osteogenesis. On the other hand, the specialized coatings can substantially improve the interaction of the implants with bone tissue cells. The most well-known bioactive material is crystalline hydroxyapatite (HA). This mineral is equivalent to the crystalline component of bones. An HA-coating on metallic implants improves adhesion of osteoblasts and accelerates formation of the bone matrix. It is proven that the surface of titanium coated with a porous HA layer provides a more dense contact “bone-implant” compared to the uncoated surface, decreasing the risk of fibrous capsule formation [6]. The cells feel the HA as their own environment: the activity of alkaline phosphatase and the expression of osteogenic genes increase, which leads to faster mineralization at the edge of the implant [7]. Another example of bioactive materials is bioactive glass (bioglass). This is Si-based material, which releases Ca^{2+} and SiO_4^{4-} during contact with the organism liquids, stimulating osteoblasts. Systematic review states that titanium implants coated with bioglass exhibit a high level of osteoblast viability and accelerated bone formation *in vivo* [8].

Besides the chemical composition of the coating material, the structural and morphological properties of the coating are also important. The roughness of the coating and its porosity increase the contact area, serving as a frame for bone growth [9]. Macroporous coatings

with pores sized 50...300 μm facilitate germination of bone beams in the implant pores, providing mechanical bonding (interpositional osteoconduction). Also, the nanorelief influences the cell behavior. It was shown in particular that nanostructured surfaces (for example, titanium dioxide nanotubes) imitate natural bone substrate and stimulate attachment and proliferation of the osteoblasts. Rajyalakshmi *et al.* demonstrated [10] that titanium implants with a layer of nanotubes 40...50 nm in diameter provide better colonization by bone cells compared to mast cells, decreasing adhesion of macrophages and local inflammation.

3.2. Inflammatory reactions and immune response

Implantation of a foreign body (material) necessarily causes an immune response. Normally, short-period controlled inflammation is a part of the healing process: neutrophils and macrophages migrate into the implantation location and clean the wound. However, excessive or chronic inflammation can lead to the formation of a fibrous capsule around the implant, isolating it from the bone and hindering osseointegration [11]. Therefore, the implant coating should minimize the undesirable inflammatory reaction and facilitate the transition of the immune system in the regeneration phase. In this case, macrophages play an important role – they can acquire an inflammatory phenotype (M1) or a regenerative one (M2). The ideal situation is when the coating material causes macrophages to M2 phenotype, which produces anti-inflammatory cytokines and growth factors, stimulating bone formation. Some coatings can modulate this osteoimmune interaction. For example, embedding of Mg ions in a titanium oxide coating leads to a decrease in secretion of anti-inflammatory mediators by macrophages and reduces expressiveness of inflammation in the surrounding tissues [12]. The coating based on special glass ceramics enriched with Mg and Sr causes depression of Toll-like receptor inflammatory pathway in cells, which manifests as a decrease in the inflammation and better integration of the implant. To decrease the inflammation, biopolymer implants are also used. For example, chitosan-based coatings are biocompatible and biodegrade slowly, having the natural anti-inflammatory properties [13]. Chitosan is obtained from chitin, serves as an osteoinductive matrix as well as can bond endotoxins and inhibit activity of anti-inflammatory factors. This facilitates the following: the long-term inflammatory process does not occur around the implant and oppositely, the phase of bone repair and remodeling begins earlier [14].

3.3. Influence on the healing processes

The implant coating can substantially influence the bone healing rate and quality after operation. Osteoconductive coatings, which serve as a frame for bone growth, can accelerate osseointegration of the implant, forming a continuous contact between the implant and bone tissue without a fibrous layer. It was proven that hydroxyapatite coatings facilitate fast growth of the bone mass on the implant surface in early periods. Under clinical conditions, this manifests itself as a higher initial stability

of cementless endoprostheses with HA coating compared to implants without coating [15]. A review shows that after several years of exploitation, the fraction of the implants with the HA coating remains stable and not smaller compared to cemented implants, indicating equal long-term survival. It also indicates that the coatings of bioactive ceramics can provide the effect of “biological cementation”, when the bone itself successfully fixes the implant [16]. In experiments on animals, the positive influence of the implant coatings was also obtained. Particularly, in rats and rabbits, implants with HA or bioglass coatings demonstrated higher areas of the bone/implant contact and higher strength of connection in mechanical tests compared to implants without coating. These positive effects of the coatings were explained by earlier mineralization of the newly formed bone and weaker bone resorption. It is especially important to achieve stability in the first weeks after the operation due to a high risk of the implant micro motions in this period. Osseointegrative coatings reduce this period, facilitating early functional loading of the operated limb in the absence of contraindications [17].

Besides the stimulation of the newly formed bone, some coatings can influence remodeling of the existing bone. For example, coatings doped with Sr can reduce activation of osteoclasts (cells which destroy the bone), holding the bone mass around the implant, which is very important for patients with osteoporosis. Also, if the implant has different mechanical properties due to the coating (for example, an intermediate layer), it can reduce the “stress shielding” phenomenon, where a high-strength implant takes all the mechanical loads on itself. In this case, the bone around the implant atrophies due to low load [18].

Therefore, a correctly selected coating facilitates the initial healing as well as supports the healthy state of the bone tissue around the implant during long term.

Generally, numerous studies confirm the following: implant coatings increase the quality of osseointegration and decrease the periodicity of aseptic rocking. In review [2], which includes 40 *in vivo* studies, the authors conclude that bioactive and antimicrobial coatings facilitate reduction of bacterial complications without negative effect on bone healing and, in some cases, demonstrate improvement in osseointegration.

3.4. Osteoinductive and osteoconductive properties

Osteoconductivity of material is the ability to serve as a frame for bone growth, while osteoinductivity is the ability to induce formation of a new bone tissue even in places where it does not occur. Most coatings applied today are osteoconductive. On the other hand, the formation of the osteoinductive properties in them is a challenge for researchers. In this case, the main approach concerns embedding of biologically active molecules (for example, the bone growth factors) into the coating. A good example is the coating with immobilized BMP-2 (bone morphogenetic protein 2). BMP-2 is an effective osteoinductor, which can initiate osteogenesis in mesen-

chymal stem cells (MSCs). Moreover, investigations also confirm the role of the BMP-2 in stimulating osteogenic differentiation in the MSCs. For example, the study showed that BMP-2 facilitates osteogenic differentiation in MSCs by increasing the activity of mitochondria, which indicates the importance of energy metabolism in osteogenesis. There are experimental examples of coatings which provide the controlled release of BMP-2 during the optimal time after implantation [19, 20].

Bioactive glass is one of the most common osteoconductive coatings. This material is well compatible with bone and stimulates formation of apatite on its surface. At the same time, bioactive glass has some advantages in osteogenic properties. Investigations show that bioactive glass coatings can induce more pronounced formation of new bone tissue compared to hydroxyapatite. The reason is the resorption of bioglass in physiological solutions with the release of Ca^{2+} and SiO^{4-} ions and other biostimulating agents, which increase the activity of osteoblasts and stimulate vascularization of the healing area [21].

However, novel deposition technologies (sol-gel, laser deposition, gas-detonation spraying) allow formation of uniform glass-like coatings with high adhesion to titanium. Hence, bioactive glass is a promising alternative to hydroxyapatite, demonstrating better osteoinductivity due to the release of ions [22, 23].

Another approach to enhance the osteoinductive properties of coatings is adding bioactive molecules or ions to the coating composition. Metal ions, namely Sr^{2+} , Zn^{2+} , and Cu^{2+} , are well-known for their positive effects on bone metabolism. Strontium, for example, stimulates proliferation of osteoblasts and simultaneously depresses bone resorption by osteoclasts. Therefore, it can be systematically applied to osteoporosis. In the case of HA coatings, partial substitution of calcium with strontium causes a substantial increase in the formation rate of a new bone around the implant [24]. A recent metaanalysis of preclinical investigations showed that implants with Sr-doped coatings had a higher (by ~19%) contact area of the bone with the implant in the osteoporotic model and substantially higher strength of fixation compared to the coatings without strontium. This effect is statistically significant and confirms that Sr-doping improves the osseointegration properties of coatings at the bone mass deficiency [25].

Other ions (zinc, silicon, and magnesium) are also studied as the active dopants to apatite and glass-ceramic layers. They can improve the activity of osteogenesis ferments and collagen synthesis rate by osteoblasts. For example, zinc is a cofactor of alkaline phosphatase. Therefore, Zr-doped coatings stimulate matrix mineralization. Copper in moderate quantities facilitates angiogenesis, which is the process of capillary growth in the implantation zone, which improves bone formation indirectly. At the same time, Cu^{2+} ions also have a direct osteogenic action. In experiments on animals, Cu-based coating of implants enhanced the bone deposition on their surfaces. However, an excess of copper can be toxic, therefore, it is important to control its content [26].

3.5. Antimicrobial properties

Inflammation of an orthopedic implant (fixation device) is a severe complication, which may cause osteomyelitis, pseudoarthrosis, and multiple revision operations. Bacterial biofilm on the metallic surface is poorly affected by antibiotics, therefore, prevention has a crucial importance. Use of coatings with antimicrobial properties aims to decrease bacterial adhesion, prevent biofilm formation, and provide local release of bacteriocidal agents during the first hours and days after implantation [2].

There are two main approaches. The first one is use of contact-active coatings, which kill microorganisms at contact with the surface. The latter can be caused by embedded biocidal groups or Si nanoparticles. The second one is use of coatings with controlled release of antimicrobial substances (antibiotics, antiseptics, metal ions) in the surrounding tissues. Some of the novel developments join both approaches, forming multifunctional “smart” coatings, which first release high doses of bactericide, then provide long-term contact protection from bacterial colonization of the implant [27].

Silver is a well-known antimicrobial element, which is used as a dopant for the implant coatings. Ag^+ ions have a wide spectrum of action: they are detrimental to gram-positive and gram-negative bacteria (including multidrug-resistant strains) and also to fungi and even viruses. The mechanism of silver action is complex: the ions destroy the cell membrane of the bacteria, bind the thiol groups of proteins and DNA, and inhibit respiratory ferments, which leads to the microorganisms death. It is worth noting that bacterial resistance to silver occurs very rarely, and formation of a biofilm on the Si-doped surface is substantially complicated. The coatings with silver can be realized as thin nanolayers sprayed on metal, which provides slow release of Ag^+ ions, or in the form of Ag nanoparticles embedded in a porous matrix. The investigations demonstrated the high efficiency of these coatings: in preclinical experiments, they almost completely inhibited the growth of *Staphylococcus aureus* and *Pseudomonas aeruginosa* and substantially reduced the formation of biofilms, simultaneously without hindering osseointegration [28].

Clinically, coatings with silver are already implemented for large-sized tumor prostheses. In this case, the results of metaanalysis of 19 studies, including 755 patients, showed a decrease in the general level of infections (to ~17.6%). The most pronounced effect in the revision cases after infections is the following. A revision prosthesis with the silver-based coating shows the infection in 13.7% cases, while using prostheses without silver-based coating, in 29.2% cases ($p = 0.019$).

Hence, the infection risk at the revision replacements decreased by 2 times due to the antibacterial action of silver. Any systematic complications (argyria outside the implantation area or organ dysfunction) were not observed for these patients [29].

Besides silver, prospective coating layers also contain Cu, Zn, Se, and other elements exhibiting antimicrobial activity. For example, Cu inhibits

reproduction of staphylococcus and is well tolerated by human cells at low concentrations. The coating with titanium nitride and copper reduces adhesion of bacteria; however, unsubstantial release of copper confined the bacteriocidal effect in this case [30].

Zinc has a bacteriostatic action and can also prevent biofilm formation. Zinc oxide nanostructures are being studied as a component of combined coatings [31]. Nanostructured selenium manifests a pronounced action against MRSA (Methicillin-Resistant *Staphylococcus aureus*), damaging the bacterial membrane. Moreover, it can be fixed on the implant surface chemically, without loss in activity.

Hence, metal-based antimicrobial coatings provide long-term protection of the implants from infections and minimize the resistance risk, which makes them attractive for clinical applications [32].

Another approach is deposition of layers on the implant, which include a high concentration of antibiotics for local release. The classical example are the gentamicin-dilactide coatings of intramedullary rods. These rods (e.g. UTN PROtect® system) are already applied in Europe for treating open fractures of tibia. The surface layer resorbs slowly, providing a bacteriocidal concentration of gentamicin in the implantation area within several weeks. In prospective investigations with a high risk of infection (III grade open fractures), use of gentamicin-impregnated nails allows for complete avoidance of deep infections. [33]. The systematic review of 8 investigations, including 203 patients, showed that the infection prevention at the primary fixation of open fractures using the rod enriched with gentamicin was achieved in ~ 96% cases (only in 3.8% cases an infection was observed, mainly in the most severe injuries). In other cases, successful use of these rods at the infected bone nonunions was reported, when high-dose local delivery of antibiotic facilitated overcoming chronic infection in 90% patients [1].

Combination of two antibiotics (for example, vancomycin + gentamicin) is also prospective. In preclinical models of open fractures with *Staphylococcus aureus* contamination, coatings with slow release of vancomycin and tigecycline almost prevent the infection progression compared to uncoated implants. Besides polymers, antibiotics can be embedded in porous ceramic coatings, namely porous calcium phosphate. The antiseptic coatings with chlorhexidine and iodophors are also interesting. The film that releases chlorhexidine on the intramedullary rod has demonstrated a decrease in the implant infection [34].

Iodine-enriched plates are used in Japan. A treatment with povidone-iodine creates a stable layer of iodine oxides on the surface of the implants, which are a strong antiseptic. In a retrospective series of skeletal oncology surgery, application of iodine-enriched tumor prosthesis shows absence of deep infections compared to the group of prosthesis without coating, where they were observed.

A summarizing analysis of a number of clinical investigations shows that each of the mentioned approaches, namely, gentamicin, silver, and iodine, significantly reduces the risk of postoperative infections compared to the coatings not enriched with antibacterial

substances. The summarized data of 7 investigations, including 1307 patients, demonstrate a ~3 times reduced infection rate by using the implants with coatings enriched with antibacterial substances ($p < 0.001$) [35].

3.6. Biodegradable coatings

Traditional coatings (HA, oxides) are designed to remain on the implant for its lifetime. However, there is a concept of temporary coatings that perform their function by resorbing, leaving no foreign material in the body [36]. Today, intensive investigations are being carried out on magnesium alloys for screws and rods, which resorb after bone union. To control their resorption rate and provide initial strength, calcium-phosphate coatings are deposited on Mg-implants. These coatings should be resorbed together with the implant or a little faster, not hindering the bone remodeling [36].

For titanium permanent implants, biodegradable coatings are also under discussion. Particularly, prospective coatings are polymers, which resorb slowly, releasing drugs. For example, polylactide (PLA) coatings enriched with antibiotics are being developed. In this case, after implantation, the PLA layer resorbs during several weeks, leaving a clean titanium surface. This allows protection of the implant during the most critical period (the first month), with further removal of the foreign material, when it is no longer needed [37].

Combined coatings with adapting properties, which can perform several functions and adapt to changes in the ambient conditions (pH, temperature, presence of bacteria), are the object of investigation today. One of these coatings is a multilayer system with inflammatory responses. For example, the coating includes a layer enriched with an anti-inflammatory drug (cytokine IL-4 or dexamethasone), releasing at an excessive inflammation, and a layer enriched with an antibiotic, which activates at a local decrease in pH induced by the bacterial infection. In normal conditions, these substances remain immobilized; however, when strong inflammation occurs, the coating releases them [38].

Another approach is a slow release of gentamicin, IGF, and BMP-2. This approach is effective for prevention of infection and stimulation of osteogenesis. Gentamicin releases quickly from the outer layer, providing antimicrobial protection. IGF-I supports cell proliferation, and BMP-2 initiates osteogenesis in later stages. The mentioned multiphase system for growth factor delivery from the implant demonstrates an additive effect, enhancing metabolic activity and osteoblast differentiation [39].

3.7. Coating deposition methods

One of the most common industrial methods is plasma spraying. In this method, powder spraying occurs in a plasma flux at high temperatures. This method has been intensively used since the 1980s for depositing HA on joint endoprostheses. The plasma spraying provides relatively thick (50...200 μm) layers with a high roughness. Modern improvements, namely application of vacuum or high rates of spraying, allow for obtaining more dense and adhesive HA layers [40].

Alternative methods are magnetron spraying or laser ablation. They provide the coatings with a high uniformity. For example, laser ablation allows obtaining the HA coating with a composition gradient, including layers enriched with silver or other ions, for combining properties.

Gas-phase methods provide precise control of the thickness and composition of the coatings, but require expensive equipment and have problems in scaling to large areas and complex shapes [41].

Sol-gel technology is a chemical deposition of the coating from a colloidal solution with subsequent polymerization (gelling) and thermal treatment. This method is good for deposition of bioactive glass and mixed oxide layers. The sol-gel method provides highly uniform and pure coatings with a thickness of several nanometers to tens of micrometers. For example, sol-gel deposition of a bioactive glass on titanium forms a smooth amorphous layer, which crystallizes into a bioactive phase under thermal treatment. In this case, an optimal treatment temperature providing the best biocompatibility is equal to 700°C [42].

Electrophoresis deposition is another method for applying coatings on complex shapes. In this case, particles of a material (hydroxyapatite or bioactive glass nanoparticles) disperse in a liquid and deposit on the implant surface under the action of an electric field. This method allows obtaining composite coatings including antibiotics and biopolymers with ceramic particles at room temperature. Usually, the obtained layer requires an additional thermal treatment to fix it to the substrate [43].

Anodizing (electrochemical etching) of titanium surface is a special case when TiO₂ nanoparticles form on the implant surface. These nanoparticles, namely nanotubes, can play the role of micro-reservoirs for embedding antibiotics and osteogenic factors. Systematic reviews show that anodized nanostructured titanium surfaces sufficiently increase the implant osseointegration in animals (the best result is observed for nanotubes with a diameter of 70...100 nm). According to a metaanalysis, nanostructuring of the TiO₂ coating increases the strength of the system implant-bone as well as the contact area. Moreover, the nanopore filling with nanocomposites (e.g. silver + biopolymer) further enhances osteogenesis.

Electrochemical methods are relatively simple and do not require high temperatures, which allows embedding thermolabile substances, namely, antibiotics or growth factors [44].

Each of these methods has its advantages and disadvantages. In particular, plasma spraying is an economical method, but the resulting coatings have limited application in medicine, as the chemical composition and crystallinity of the coating change significantly, which does not guarantee the required service life of the coating in the body. It is characterized by poor adhesion and non-uniform thickness. The sol-gel method ensures chemically uniform films, is simple and inexpensive, but requires additional heating of the part to 300...700 °C to remove precursor components, which is often unacceptable because it deforms the part and deteriorates its mechanical properties. The films

typically have unsatisfactory mechanical strength. Laser deposition allows for creation of high-quality films with good adhesion, but their chemical composition may differ from stoichiometric. Electrochemical deposition allows for coating objects of irregular shapes at low temperatures, but the layers are characterized by low adhesion [45].

One of the best deposition methods is gas-detonation spraying (GDS) [3–5]. GDS addresses many applied problems related to obtaining functional coatings for both the medical field and other sectors of the economy and the military. The developed method allows for applying coatings with the required thickness and roughness, good adhesion to metals and polymers, and other necessary physicochemical parameters for specific applied tasks. The essence of the developed GDS method lies in the use of the energy of propane-oxygen mixture explosions, which accelerate powder particles used to form coatings to speeds several times higher than the speed of sound. The particles then form a coating with the chemical and phase composition similar to the original powder upon inelastic collision with the surface of the part (implant). The main advantages of this method, among others, include:

- a) High productivity, the ability to apply layers of varying thickness (from a few microns to millimeters) on large-area substrates (up to several square meters) and complex surfaces.
- b) The ability to use powder mixtures made from multiple components to create a composite.
- c) Control of the kinetic energy of explosions by varying the percentage content of the explosive gases.
- d) Application of the same method for preparing the substrate surface for coating formation (abrasive powder mechanical cleaning, creating micro-relief on the surface).
- e) The ability to change the deposition parameters in a controlled manner to vary the coating characteristics, achieving high microhardness with good adhesion to the substrate.
- f) Parts are not subjected to thermal mechanical deformation due to the short duration of explosive gas action. The ability to apply multi-layer coatings with different chemical compositions.

3.8. Future directions of investigation

One of the main trends is the development of multi-functional “smart” materials for coatings, which combine osseointegrative, anti-inflammatory, and antimicrobial properties. Modern investigations have focused on materials never applied in orthopedics. Graphene and graphene oxide are new carbon materials, which are prospective as an addition to coatings due to their high mechanical strength and antibacterial properties. Addition of a small quantity of graphene oxide to an HA coating increases the strength and initiates a bactericidal effect due to mechanical damage of bacteria by the sharp graphene sheets. Simultaneously, HA coating enriched with graphene oxide stimulates osteogenic differentiation of stem cells through modulation of macrophages [46].

Metal-organic frames (MOF) are another type of orthopedic materials. These are crystalline porous materials which can accumulate and release biologically active molecules. They are tested as coatings with slow release of antibiotics and act as a “sponge” for toxins. For example, MOF based on zinc and bisphosphonates can slowly release zinc and inhibit growth of bacteria [47].

Biomimetic composite materials are also studied. It is well known that the bone is a composite of mineral and polymer (collagen). Therefore, polymers (collagen, chitosan, hyaluronic acid) combined with bioceramics (HA, bioglass) is a logically correct approach. These materials can better imitate an extracellular matrix and initiate acceleration in regeneration. A successful example is the coating of collagen impregnated with HA. In this case, collagen provides elasticity and binds growth factors, while the HA provides hardness and bioactivity [48].

Polydopamine is a polymer based on seashell glue that has the property of a universal adhesive layer. It can be easily deposited using polymerization from dopamine on any surface and can bind metal ions, proteins, and DNA. In coating technology, it is used for fixation of coating components to the implant. For example, Ag nanoparticles can be fixed in a dopamine layer on the implant, forming a long-term antibacterial coating. Also, polydopamine can play the role of a carrier of growth factor (BMP-2), forming a double coating (PDA + BMP-2) for osteoinduction and a surface silver layer protecting against bacteria [49].

3.9. Limitations

Most of the modern investigations on the functional coatings of orthopedic implants are based on *in vitro* experiments or on experiments on animals, which limits generalization of the results and does not allow for formation of a sufficiently convincing evidence base for widespread clinical implementation. Significant variability in the deposition methods, physical and chemical properties of coatings, and conditions of their study complicate comparison of separate studies and formation of uniform application protocols.

Despite the high prospectivity of the novel materials, particularly graphene, MOF, and nanocomposites, as well as combined multifunctional systems, most of them are in the stage of laboratory and preclinical studies, without sufficient clinical results. Another problem is the difficulty of industrial scaling of the methods for coating deposition on implants with complex shapes, which require further optimization and standardization of technological processes. In this case, the implant coatings are a prospective but still experimental approach for the improvement of the results of orthopedic surgeries, which requires careful verification in controlled clinical investigations and long-term monitoring of their safety and efficacy. Future investigations should be focused on clinical evaluation of combined osseointegrative and antimicrobial coatings involving models of osteoporosis and infected defects.

4. Conclusions

The development of coatings for orthopedic metal fixation devices leads to an increase in the efficiency and safety of osteosynthesis. Novel coatings based on hydroxyapatite, bioactive glass, doped compositions, and nanomaterials can substantially improve the biocompatibility of implants and stimulate osseointegration. Analysis of the modern investigations confirms that the coatings of the orthopedic implants with bioactive and antimicrobial materials can substantially improve clinical results of osteosynthesis. Hydroxyapatite, bioactive glass, Sr-doped coatings, and compositional systems based on graphene oxide or polydopamine demonstrate pronounced osteoconductive and in some cases, osteoinductive properties. They enhance adhesion of osteoblasts, accelerate mineralization, modulate the inflammatory response, and reduce the risk of aseptic rocking.

On the other hand, the coatings enriched with silver, iodine, gentamicin, chlorhexidine, or microelements (zinc, copper, selenium) provide local antimicrobial protection, reducing the rate of biofilm formation and purulent complications without inhibiting tissue regeneration. Modern multifunctional coatings can combine several functions, namely antimicrobial, osteogenic, and anti-inflammatory. They can be tuned to specific clinical tasks. The best results can be achieved by combining osteo- and antimicrobial properties in one implant. Novel investigations are focused on multifunctional and smart coatings, which can simultaneously facilitate bone regeneration and protection against infection.

Solving technological problems of the deposition of the mentioned coatings on complex surfaces, as well as collecting clinical experience, are the key directions for the coming years. With account of recent progress, the coatings of orthopedic implants can potentially be integrated into clinical practice, be an integral part of treatment standards, increasing the percentage of successful healing of complex fractures and reducing the number of reoperations. The latter ensures better results for patients and reduces the load of orthopedic diseases on the healthcare system.

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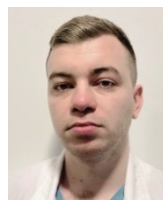
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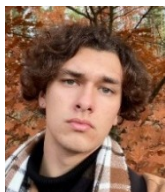
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Біоактивні покриття металевих ортопедичних імплантатів: функціональні властивості та клінічний потенціал

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Анотація. Застосування металевих ортопедичних імплантатів (гвинти, пластини, інтрамедулярні стрижні) супроводжується такими проблемами, як недостатня біологічна інтеграція та високий ризик інфекційних ускладнень. У даному огляді узагальнено сучасні дані щодо функціональних покриттів металевих ортопедичних імплантатів, зокрема їх остеоіндуктивних, остеокондуктивних, імуномодулюючих і антимікробних властивостей, а також оцінено потенціал їх клінічного застосування. Основними біоактивними покриттями, які розглядаються в роботі, є гідроксиапатит і біоактивне скло, а також наноструктуровані та леговані шари. Проаналізовано методи нанесення покриттів, зокрема плазмове напилення, золь-гель технологію, анодування та електрофорезне осадження, газово-детонаційне напилення. Встановлено, що покриття з гідроксиапатиту та біоактивного скла значно покращують біосумісність та стимулюють osteointegration. Легування іонами (стронцій, цинк, магній) підсилює остеоіндуктивні властивості покриттів, а наноструктурування підвищує адгезію клітин та послаблює запальні реакції. Антимікробні покриття зі сріблом, антибіотиками й бактерицидними речовинами ефективно знижують частоту інфекційних ускладнень. Найбільш перспективними для промислового використання є плазмове напилення, золь-гель технології і газово-детонаційне напилення. Багатофункціональні та «розумні» покриття демонструють високу клінічну ефективність і перспективи широкого впровадження. Подальший розвиток технологій нанесення та оптимізація складу покриттів дозволять зменшити ускладнення й покращити результати лікування пацієнтів з травмами та дефектами кісток.

Ключові слова: біоактивні покриття, ортопедичні імплантати, методи осадження, біологічна інтеграція, ризик інфекції.