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COATINGS IN ARTHROPLASTY

Review Paper

ABSTRACT

The modern coatings used in arthroplasty for long term implants are reviewed. The phosphate coatings are the most popular technique to improve the bone-implant interfacial strength and promote the osseointegration. The plasma spraying, electrophoretic precipitation, powder metallurgy, ion beam sputtering, high velocity oxy-fuel (HVOF) combustion spraying, sol-gel technique, biomimetic deposition are mostly used to obtain the phosphate, usually hydroxyapatite coatings.
The composite coatings based on HA are proposed to improve biochemical and mechanical properties. The Ti, Ti alloys, titania, zirconia, zinc particles and glasses are suggested to strengthen the HA matrix, and some organic compounds and polymers to improve the biochemical behaviour.
Among another coatings, titania, zirconia, aluminia, carbon and organic, glass – ceramics and titania – silicate coatings are mostly proposed.

Key words: *coatings, hydroxyapatite, biocompatibility, bioactivity*

PHOSPHATE COATINGS

General characteristics

The deposition of phosphate coatings is nowadays one of the most popular technologies used to increase biocompatibility of metallic implants. Another aim of their use is an increase of adhesion strength between an implant and a bone. The phosphate coatings are deposited on cementless implants used in orthopaedy and stomatology [1,2]. They are technical solution allowing for direct bonding of implant and bone, easier and stronger implant fixation, diminution of pain level. As the incomplete bonding of bone and implant surface is a main problem in total hip arthroplasty THA, the application of phosphate coatings becomes here a usual procedure.
The phosphate coatings used in arthroplasty are, based on their chemical composition, hydroxyapatite (HA) $Ca_{10}(PO_4)_6(OH)_2$, apatite (AP), carbonate apatite (CAP), octacalcium phosphate (OCP), tricalcium phosphate (TCP). The phosphate coatings have many features deciding on their appropriateness and quality. They include: chemical and phase composition, thickness, crystallinity degree, resorption ability.

Particularly, adhesion strength of the implant to a bone is the main property which decide on resistance to cracking and delamination. The crystalline coatings demonstrate low dissolution *in vitro*, low resorption and more direct contact to a bone. High content of amorphous phase may provoke a rapid weakening and disintegration of coating, promoting inflammation of an adjacent tissue. On the other hand, a certain low amount of amorphous HA can stimulate better physiological activity by enhancement of reprecipitation of amorphous HA or addition of certain proteins [1,2]. In an assessment of biocompatible and osteogenic properties [3] of biphase CaP in granules with an use of primary human cultures of osteoblasts and monocites it has been established that at higher TCP content, 80% and 100%, affected negatively cell adhesion. At 20 and 50% the control of inflammatory reaction has been initiated.

The presence of CaP seems necessary because of the perfect biocompatibility of phosphate ceramics, its mechanical properties, a substantial enhancement of bone in-growth and better quality of formed bone tissues. As to initiate the bone growth, the presence of bi-phase phosphate ceramics is mostly preferred but after 8 weeks period from implantation the deposited OCP seems also sufficient [4]. The dissolution of titanium with deposited HA causes likely incorporation of Ti ions and formation of Ca titanate [5]. Hydroxyapatite [6] demonstrates the highest value of alkaline phosphataze and Ca in bacterias culture, expression of gens of osteopontin and bone sialoprotein, mineralized module formation.

Despite that the HA coatings are almost exclusively formed on Ti and its alloys, this technique may be also developed for other metals.

The stainless steels can be covered with the HA coating. Sol-gel technique brings out [7] nanoporous structure with adhesion strength 44 MPa. Dense and well adjacent coatings are formed after short annealing at 400°C.

Tantalum has been also proposed to cover with the apatite coating [8]. The treatment has composed of immersion in water > 5 M NsOH solution at 95°C for 24 h followed by immersion in simulated body fluid (SBF). The formation of apatite is highly accelerated by NaOH treatment and annealing at 300°C. After such treatment an amorphous Na tantalite, and without alkaline treatment – passive Ta oxide.

The apatite coating has been also applied for metalic Zr [9]. The Zr gel has been formed in which Zr-OH group facilitated apatite nucleation.

Important problem is effect of presence and properties of HA coating on bone in-growth. Comparing bone pull-out strength on implants with plasma sprayed HA and Ti, in *in vivo* studies on dogs [10] no special difference was found but the bone contact length was higher for coated implant. The HA coating behaves similarly to glassy ceramics and better than pure Ti as differentiation of osteoblasts and mineralized tissue formation is considered [6].

The clinical successes of HA coated implants paid attention to *in vivo* behaviour of the coatings. After 6 months from implantation the HA coating disappeared. The metallic surface bond to the bone was similar to that of uncoated implant. The HA degradation is then fast and such coating has no importance in long term behaviour [11].

The *in vivo* behaviour depends on topography and crystallinity [12]. In examinations of hip joint HA coated endprosthese, after removal of implants the good adhesion to the bone was observed only on rough areas and not on the smooth ones.. The structure of coating varied from totally crystalline for vacuum plasma sprayed coatings to partly crystalline for air plasma sprayed coatings. However, in the last case the cracking initiated from amorphous phase was observed.

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Coating thickness is important feature. The bone – implant total length is larger when the thin coating obtained by biomimetic methods is applied as compared to thick classical coatings obtained by plasma spraying and thermal modification or surfaces sand-blasted with titania and next etched in 10 % HF + 5% HNO_3 mixture [13].
The presence of coatings is substantial at fabrication of porous implants. The HA coating obtained by sol-gel method causes in *in vivo* examinations increase in absolute contact lentgth in bone – implant area and area of bone in-growth [14].
The increase in osseointegration can be obtained by surface treatment with short pulse excimer Cr-F laser [15]. Such solution results in doubling the actual surface area and change in its topography to columnar or cone shaped allowing better reactivity.

Fabrication techniques

There is a number of deposition technologies of phosphate coatings. They include: chemical precipitation, electrophoretic deposition, hot pressing, ion beam sputtering (with ion beam assisted deposition IBAD mostly used), plasma spraying, conventional flame spraying, *high velocity oxy-fuel (HVOF) combustion spraying*, sol-gel technique, biomimetic deposition.

Plasma spraying

The plasma assisted depositions by air or vacuum spraying are very popular as they allow obtaining the coatings assumed to have relatively good mechanical properties. On the other hand, they often demonstrate a weak tensile and fatigue strength. Therefore some modifications of both techniques have been proposed.
The titanium surface has been covered by spraying with apatite powder for 10 s followed by ultrasonic cleaning in order to remove loosely adsorbed powder [16]. In such conditions better apatite adhesion, lack of inflammatory reactions, strong bonding of bone and implant, and better ostecoconductivity are observed.
Mechanical properties of HA coating highly depend on its thickness. The 150 μm coating deposited on the Ti-6Al-4V alloy by plasma air spraying substantially decreases fatigue strength, and 25-100 μm do not show such an effect [17,18]. The possible sources can be: intrinsic stresses generated during spraying, cracks propagating across the coating, stresses liberated during spraying, the most significant. The difference in rigidity of coating and bare metal seems also important.
More popular is now plasma vacuum spraying. The increasing plasma power results in decreasing crystallinity degree and content of hydroxyle ions in the coating. It is not positive phenomenon but it can cause the decrease in porosity and number of cracks, increase in Young modulus and adhesion strength. Generally, the Young modulus value is low, < 6 GPa, and much lower at tenson than at compression, following presence and opening of cracks. The intrinsic stresses comprise between 20 and 40 MPa and can cause formation of cracks propagating across the coating [1]. Delamination can likely occur also as an effect of compressive strains as the coating – base strength is relatively low, below 20 MPa [19].
Deposition of HA coating by plasma spraying creates the biaxial intrinsic compressive stresses of Young modulus 6 or 16 GPa, depending on measurement direction [20]. This is much below 34.5 to 120 GPa, obtained for sintered coatings. Therefore 50 μm thick coating may be permitted, and 200 μm thick is coating assumed as unstable. On the other hand, an assessment of Young modulus in HA coating, 90-200 μm thick, showed

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95 GPa value at 80% crystallinity degree and 71 GPa at 10% mas. [21] so that much more than previously.

During air plasma spraying the thin zone of amorphous phosphate (ACP) is formed close to the surface [22]. After 1 week of immersion in Simulated Body Fluid (SBF) some diffusion bands are formed inside the ACP zone, 1-2 μm thick, parallel to the interface, presumably because of dissolution and precipitation processes.

The heat treatment is sometimes proposed to improve the structure and properties of the HA coatings. Annealing of HA coating at 400°C for 90 h promotes the transformation of partly amorphous coating into crystalline one [17,18]. The thickness and colour of the coating change, fatigue strength decreases.

Generally, high crystallinity degree of the HA coating is assumed to be a good property. It usually ranges between 65 and 70%. As to obtain highly crystalline coating, in plasma spraying technique the fully crystalline HA is used as a substrate. Rapid solidification during spraying limits a number of formed crystals, and additionally oxyhydroxyapatite (oxidized HA) is formed, less prone to form crystalline structure. During spraying the decomposition of HA into a mixture of α-TCP (that may further transform into β-TCP at 1000°C or remain in the coating as a stable phase) and tetracalcium phosphate TTP or CaO at temperature above 1400°C [1].

It may be especially important for key value of toughness at interface. During and after spraying the mechanical coupling of the coating and base metal interfaces occurs even if chemical adhesion due to diffusion of elements cannot be excluded. The toughness value at interface has been estimated at very low value 1-10 J/m^2 [1]. This may effect in localization of metal-coating fracture at interface. As the way to improve adhesion, the deposition of thin sub-layer of Ti onto the rough base or sub-layer of porous Ti has been proposed [1,2].

Annealing at 700°C for 1 h results in increase in crystallinity degree, hydroxyl ions and coating purity but in adhesion decrease at high spraying power values, at which the amount of formed amorphous HA is especially great [1,2]. The transformation of amorphous HA into crystalline HA causes an appearance of tensile stresses followed by possible cracking at annealing at 600 lub 700°C, as an effect of volume changes. The best procedure can be then plasma spraying at high power in gas, deposition of sub-layer of titanium and annealing at 700°C.

The observations of HA and Ti mixture suggest that during annealing at 1100°C in vacuum the hydroxyle groups are lost and secondary β phase is formed. The metallic Ti disappears and the complex oxide of Ti and Ca appears. That suggests transformation of mixture of metal and ceramics into composite ceramics [21].

The problem can be an achievement of high adhesion. The increase in bond strength may be reached by chemical bonding with an use of coupling agent. As such compound the Ca silicate has been proposed, as a 10-50 μm thick coating on the Ti-6Al-4V alloy. Such solution gives an increase of bond strength above 30 MPa. The promising may be coatings composed of eutectics of Ti oxide and non-stabilised Zr oxide, on which the HA coatings have been deposited by plasma spraying [23]. Chemically stable layers form better barrier against release of ions from metallic implant at action of SBF. Simultaneously, thin layers of Ca and metals are formed after exposure, increasing adhesion.

HA coatings are deposited for better osteointegration but they may deteriorate corrosion resistance. For the Ti-6Al-4V alloy the increase in corrosion rate and passivation current even a row of magnitude have been observed after plasma spraying [24]. Thickness of HA coating has an obvious effect on release of ions from the alloy [25]. The 50 μm are

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ineffective in retardation of dissolution, and 200 μm coatings may substiantially prevent dissolution. As the solution, the creation of metallic phosphates on the HA coating has been proposed.

Ion beam sputtering

The HA coatings may be deposited by ion beam dynamic mixing with pure HA as a target [26]. The formed coatings are amorphous, their adhesion to the base metal increases with current value, and dissolution rate decreases. The effect is attributed to the Ca/P ratio which without IBDM is far from stoichiometric value 1.67.

Powder metallurgy

Remelting (sintering) of deposited HA is another proposed technology [27]. For three different consolidation conditions at HA coating creation on the Ti-6Al-4V alloy, at 700 °C for 5 h, 700 °C for 8 h and 700 °C for 11 h, in first case a poor mechanical anchoring has been observed. The biodissolution in SBF has been noted followed by precipitation of apatite.
The sintering at much higher temperature 1150°C has been also investigated. The porosity has been 35-48%, and pore size 50-300 μm. After application of porous HA as a substitute of bone graft [28] for tibia in knees for patients with ostearthritis, total incorporation occurred without any inflammatory processes. The pores have been filled with regenerated bone, bone in-growth succeded slowly.

Sol – gel technique

The sol-gel technique relies on forming on the metals of colloidal coatings followed by their heating in order to obtain crystalline structure. For a Ti-Mn alloy, with 6 wt. pct of manganese [29], which possesses thermal expansion coefficient close to that of HA, especially high adhesion was observed for coating deposited by sol-gel technique. The formation of Ti gel onto the surface is achieved in a simple manner as a result of chemical reaction of Ti and a mixture of 8.8 M H_2O_2 and 0.1 M HCl at temperature 80°C [30]. Long term chemical reaction, up to 1 h, gives 1 μm thick layer. An annealing brings out a gradual transformation of gel into crystalline structure: atanase at > 300°C and rutile at > 600°C. Above 700°C the densification of coating occurs. Such coatings are bioactive and able to accept apatite.
The Ca-P coatings may be obtained by sol-gel technique with an use of organic or inorganic precursor. The 1-1,5 μm thick coatings demonstrate high bond strength: 347 MPa with inorganic compound and 280 MPa with organic compound [31].
The deposition of HA coating by sol-gel technique can be facilitated with TiO_2 buffer [32]. The buffer was proposed to make the bond between HA and Ti stronger as well as to prevent corrosion of Ti. As to fabricate TiO_2 sol, the hydrolysis of titanium propoxide in ethanole mixed with diethanoloamine. The HA sol was obtained from precursors of Ca nitrate and TEP. The oxide layer 200 nm thick was fabricated and then HA coating 800 nm thick. The layers had very good adhesion, and the presence of oxide layer improved the adhesion of HA coating. The highest strength of multiplex coating was 55 MPa after heating at 500°C. The corrosion rate was lower and activity of alkaline aminophosphatase higher than for pure Ti or TiO_2 layer. The sol-gel technique has been also developed for complex fluor-hydroxyapatite on zirconia substrate [33].

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Electrochemical deposition during oxidation

The fabrication of phosphate coatings may occur simultaneously with electrochemical oxidation. In electrochemical oxidation the phosphate or Ca ions containing electrolytes, or generally SBF, are used to develop the phosphate coatings. However, as shown by in vivo investigations in rabbits, the bonding of a bovine with an implant after such procedure is wide but not especially strong. The reason may be low porosity and precipitation of apatite-like deposits inside the pores of an oxide layer [34]. In calcification supersaturation solution (CSC) the apatite coating is very close to the natural apatite [35].
After an application of the electrolyte containing 0.025 M Ca biphosphate, 0.75 M Ca acetate, 0.12 M NaEDTA and NaOH, the coating with Ca/P = 1.3 is formed, lower than in conventional electrolytes. Such coating has better mechanical stability and is composed of partly or totally dissolved CaP phase in the matrix of amorphous and crystalline anatase [36].
The application of microarc oxidation results in increase in Ti biocompatibility as demonstrated by increasing activity of alkaline phosphatase of osteosarcoma cells and decreasing proliferation [37]. The *in vivo* tests show three fold increase in bone – implant strength. Similarly, anodizing in mixture of glycerophosphate and Ca acetate at 50 mA/cm^2 current density gives the 5 μm [38] thick coating which does not improve the bone in-growth *in vivo*. Further hydrothermal treatment at 300°C for 2 h results in a layer of crystalline HA 1 μm on the previous coating.
The micro-arc oxidation at potential of 250-500 V in electrolytes containing organic compounds permits to obtain the Ca and P containing coatings, at the highest voltage - $CaTiO_3$, β-$Ca_2P_2O_7$ oraz α-$Ca_3(PO_4)_2$. After immersion in human plasma blood model solution, during 28 days the carbonate hydroxyapatite is formed. At higher content of several compunds the incubation time of HA is shortened and it is formed at oxidized surface even at lower potential, 350 V [39].
The deposition of apatite is observed on titanium oxidised anodically or thermally [40] after immersion for 7 days in Kokubo`s SBF (142.0 Na^+, 5.0 K^+, 1.5 Mg^{2+}, 2.5 Ca^{2+}, 147.8 Cl^-, 4.2 HCO_3^-, 1.0 HPO_4^{2-} and 0.5 SO_4^{2-}). The highest deposition occurs on titanium oxidized at 400 or 500°C. The apatite do not form without oxidation, and after anodisation in H_3PO_4, H_2SO_4 or acetic acid the deposition is very low.

Biomimetic methods

Biomimetic techniques are the currentless deposition of phosphate coatings on the metallic surface in their chemical reaction with physiological solution. As an example, such coating is formed after immersion of the metal in Koubo solution in order to promote nucleation of Ca phosphate and then in a special calcification solution as to obtain OCP [4].
Precalcification has got positive influence on Ti bioactivity. At precalcification by immersion for 3 days in boiling $Ca(OH)_2$ the uniform coating of carbonate apatite is formed [41].
Chemical Ti treatment substantially influences the biomimetic appearance of apatie. An exposure in NaOH results in dissolution of passive film and formation of amorphous layer rich in Na ions. They are liberated during the exposure in SBF; hydronium H_3O^+ ions enter the amorphous layer forming the Ti-OH groups. The free sodium ions increase the local solution supersaturation and then pH value, and Ti-OH groups initiate

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nucleation of apatite on the Ti surface. Previous etching in HCl gives the uniform Ti surface, of higher microroughness [42].
The biomimetic phosphate coating may be obtained using the self-assembled monolayer (SAM) technique. The Ti foil is oxidised in 50% H_2SO_4 and 30% H_2O_2 mixture for 1 h and then dried. The monolayer is obtained in the solution of silan in pentane. Further stage may be the subsequent exposure in various solutions permitting to appear the hydroxyle, carboxyle and phosphoryle groups within the monolayer, to nucleate the Ca phosphate and to deposit the phosphate coating in SBF. The deposition of Ca phosphate is accelerated in presence of monolayer with the above groups [43].
The formation of biomimetic Ca-P coatings was observed even in 24 h in SBF. In 5x concentrated SBF the formation of biomimetic Ca-P coatings was observed during 24 h. The Mg ions more and hydrocarbonate ions less enhanced preferred incubation and growth of coating onto the surface [44].
The nanoscale plays an important rule in nucleation and growth of calcium phosphate formed by biomimetic method in SBF on titanium implants [45]. The hereterogenous nucleation of Ca-P occurs instantaneously on titanium and does not depend on topography of the Ti-6Al-4V alloy. The mechanical adhesion of coating depends, on the other hand, on topography, and higher roughness, < 0.25 μm, is more favourable, then < 0.10 μm.
In [46] the deposition of apatite in 36.5% SBF for 4 weeks was preceded by alkaline treatment in 10 M NaOH at 60°C for 24 h and then heating at 600°C for 1 h. The apatite layer was bone-like and substantially increased the bending strength of an implant.
The bioactive surface of the Ti-6Al-4V alloy can be also obtained by incubation on boiling alkaline solution [47]. Such surface after immersion in oversaturated calcification solution is covered with Ca-P, presumably by previous formation of TiO_2 with a great number of submicron pits, serving as incubation sites.
As promosing alternatives of plasma sprayed HA, the biomimetic deposition of octacalcium phosphate OCP and carbonate apatite BCA, and electrolytic deposition of carbonate apatite ECA was considered. The obtained OCP is fully crystalline, 40 μm trick, composed of large platelet crystals, smooth surface. The BCA is in 60% crystalline, up to 30 μm thick, composed of small crystals, rough surface. All coatings quickly dissolve in acidified SBF, and slowly and partly in neutral solution. The best goat bone marrow stromal cells attachment was demonstrated, in decreasing order, by BCA, OCP and ECA [48].
The high temperature oxidation can be the first step to obtain the phosphate coating. As an example [49], oxidation at 400°C for 24 h of the Ti-29Nb-13Ta-4.6Zr alloy forms the hard oxide layer at the surface. Next, the oxidized samples are immersed in 10 M solution of NaOH at 60°C for 24 h. After immersion in SBF and calcifiyng solution the growth of very hard calcium phosphate layer is observed.

Laser ablation

The new technique for obtaining the thin HA coatings is pulse laser ablation with hydroxyapatite as a target [50]. The deposition of osteoblasts is accelerated by further annealing at 575°C. The new direction of surface engineering is to use of hybrid methods, which allow to produce "composite layers" with thin coating of HA with better adhesion to bulk material than regular HA coatings, and laser ablation is one of the best to produce such layers.

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The laser ablation techniques may be used for obtaining not only HA but TCP and ACP as well [51]. The amorphous ACP coating is insoluble in human plasma blood and deposition of the phosphate does not occur on the surface of the Ti-6Al-4V alloy.

CVD technique

The CVD technique with an use of metaloorganic compounds permits to obtain nanocrystalline titania layer [52] for orthopaedic and stomathology purposes. The base is decomposition of oxidized compounds (pre-cursors) or reaction of oxygen-free metals with oxidizers in low vacuum. Such layer increases osteointegration rate of commercial titanium implants and bone mineralization.

PHOSPHATE COATINGS WITH ORGANIC COMPOUNDS

During obtaining phosphate coatings from solutions, an addition of various organic compounds is often applied, especially of proteins. The proteins are important species for implantation process and, on the other hand, may influence the mechanism of creation of coating.
The HA coating may contain the veal serum protein. Such effect is reached by electrochemical co-precipitation of protein and calcium compound covered with HA [53]. This technique allows for 7x fold increase in protein adsorption as compared to an susal protein adsorption.
The bovine serum albumin BSA is essential for apatite deposition. The deposition may occur during immersion in Hanks solution for 1-23 days. The deposition does not occur in solution containing only proteins but an use of mixed solution results in thin porous film composed of protein and Ca-P [54].
The direct interaction of Ca and P is observed in apatite forming the coating on Ti with serum protein [55]. The low Ca content carbonate apatite was prepared by Ti precalcification in $Ca(OH)_2$ solution followed by immersion in oversaturated Ca-P. During immersion of coating in bovine serum the protein adsorption on surface of coating occurred, and Ca and phosphate ions dissolve and precipitate again, resulting in protein containing apatite.
An interesting proposal is an incorporation of biphosphonate being a medicine against osteoporosis within the HA coating [13]. The essential contact of an implant and a bone was observed for implants with immobile phosphonate in 12 weeks after surgery.

HYDROXYAPATITE – Ti COATINGS

One of the promising fabrication technique is sol-gel metod. The bioceramic composite on titanium obtained by such technique [56] was composed of colloidal titania particles and submicron HA particles.

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Another technique is plasma spraying. The investigations of bond strength in such coatings [57] demonstrated positive effect of Ti presence and also bioactivity after immersion in SBF.
New biocompatible multilayer coating was obtaied by alternative deposition of Ti and HA layers by radio frequency magnetron cathodic sputtering [58]. The inner layer was composed only of Ti, and outer layer – only of HA. Good adhesion and better electrochemical behaviour was shown. The coating was mostly crystalline and insoluble in SBF, adhesion was above 60 MPa, even after 14 weeks from immersion.
The in vitro studies of osteoblasts in presence of sol-gel composite coatings Ti/HA showed no cytotoxicity [59]. The ALP (alkaline phosphatase) activity and collagen production on the coating was substiantially higher on the coating as compared to those on uncoated Ti and PE (polyethylene). The HA:Ti ratio is an important factor: the best results were obtained at 1:1 ratio.
In [60] biocomposite was successfully fabricated from hydroxyapatite and titanium powders by powder metallurgy method. Main crystal phases of the as-fabricated composite are found to be $T_{i2}O$, $CaTiO_3$, CaO, a-Ti and a TiP-like phase. When the composite is immersed in SBF, a poor-crystallized, calcium-deficient, carbonate-containing apatite film starts to form on the surface of the composite within 2 h. In addition, the apatite is also incorporated with a little magnesium and chlorine element. Ti_2O has the ability to induce the formation of bone-like apatite in the SBF, and dissolving the CaO phase could provide favorable conditions for the apatite formation, by forming open pores on the surface of the composite and increasing the degree of supersaturation of the SBF with respect to the apatite.

HYDROXYAPATITE – TITANIA COATINGS

The co-precipitation of titania and crystalline Ca phosphate can be carried out by sol-gel technique [61]. The reduction in coating thickness and increase in roughness improves a quality of interface. The sol-gel technique can be applied to obtain the titania – HA composite coating [56] by an use of a mixture of colloidal particles of titanium oxide and submicronic HA particles. After drying and repetead heating at 500°C the chemically pure, homogenous, rough, porous, thin and well adjacent to HA base coating was obtained. The accelerated deposition of CaP is achieved [62] by further passivation in 0.1 M NaOH followed by an exposure in 0.5 N Na_2HPO_4 for 1-16 h and next in saturated $Ca(OH)_2$ for 5 h.
The plasma spraying is also usable for obtaining the composite coating. In a such way the duplex layer can be fabricated [63], composed of inner layer 50% HA + 50% TiO_2, and outer layer being pure HA.
Another technique used to obtain the HA – titania composite coating, can be high velocity oxy-fuel HVOF [64]. The chemical reaction between mechanically stirred HA and TiO_2 powder and $CaTiO_3$ formation occurs at temperature about 1410°C which is reached at the metal surface at the impingement moment.

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HYDROXYAPATITE – GLASS COATINGS

The composite HA - glass coating can be obtained by conventional burning technique. The Ti or Ti alloy base is covered with HA layer containing glass. In such a case the numerous pores and agglomeration od HA particles may occur, and coating has no strength sufficient to work in clinical applications and under high load. The Cullet technique relies on preliminary burning of HA + glass composition for 5-10 min. in order to achieve well homogenous powder, followed by etching in HNO_3 + HF mixture to obtain well developed and bioactive surface [65].
The dense HA ceramics are useful bone substitutes but they degrade too slowly. The addition of bioactive glass enhanced biodegradation in SBF [66].

HYDROXYAPATITE – ZIRCONIA COATINGS

Such coatings obtained by sol-gel technique show the cracking within the coating and at the coating – metal interface. As to increase the cracking resistance, the creation of composite coatings strengthened with ceramics grains seems useful, e.g. addition of 10% ZrO_2 content results in good bond between oxide and phosphate [67].
In another approach the coating composed of HA and YSZ (yttrium stabilised zirconia) was obtained by plasma spraying [68]. After immersion in SBF the carbonate apatite appeared after 4 weeks. The mechanical properties of coating decreased up to 56 days of exposure. The slight change was observed after supersaturation with Ca ions and crystallization of Ca phosphate. Anyway, the mechanical properties of composite coating were higher than those of pure HA.
Another solution is an application of composite of HA, YSZ (yttrium stabilised zirconia) and Ti-6Al-4V alloy powder [69]. The plasma sprayed coatings demonstrate high microhardness, toughness and bond strength, mainly due to zirconia. The annealing at 600-700°C up to 12 h results in increase in Young modulus about 17%. This beneficial effect can be attributed to common solid solution of all elements and dispersion strengthening by zirconia particles.

HYDROXYAPATITE – TITANIUM ALLOY COATINGS

The coatings composed of 50% of HA and Ti-6Al-4V powders can be obtained by plasma spraying [68,70]. Their density is higher than of pure HA, close to 3.89 g/cm^3, and porosity 15.82%. The disadvantage is a presence of small cracks at the surface and interface. The bond strength is estimated at 27.83 MPa with 28.46 MPa for pure HA coating. After immersion in model human blood plasma after only few hours the composite coating is dissolved and roughness increases favourising incubation of apatite nuclei. After long immersion the new island-like layer is formed, with numerous microcracks up to 100 nm. As a result of reaction between fluid and composite coating, CaO is completely dissolved, The mechanical properties decrease less than for pure HA

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coating. Annealing of composite coating at 600°C for 6 h facilitates transformation of amorphous to crystalline phase.
The sintered Ti-6Al-4V/HA composite obtained at 1100□C have high density and microhardness, at 50% porosity [71].
The composite coating HA/Ti-6Al-4V obtained by ceramic slurry miting with an use of plasma spraying was examined after 8 week immersion in SBF [72]. The tensile strength of such composite coating was higher that that of pure HA even after such exposure. The exposure resulted in dissolution of Ca-P phases even after 24 h followed by formation of carbonate apatite after another 2 weeks.

HYDROXYAPATITE – ZINC COATINGS

The serious danger for the HA coatings may be the tearing off due to HA particles from amorphous coating during bone remodelling and release of Ca-P powder even for dense HA. The interaction between HA powder and human monocites results in liberation of inflammatory cytokines. The addition of 0.5-2% Zn was proposed to retard the inflammatory processes [73].

HYDROXYAPATITE – POLYMER COATINGS

HA can be used as a scaffold. As an example, porous HA was filled in with a composite of HA and polycaprolactone (PCL) with an addition of tetracycline [74]. The HA scaffold had porosity about 87% and pores sized at 150-200 μm. Such porous structure makes blood circulation easier and permits drugs to reach the surface. PCL improves resistance to brittle fracture and strength properties. The coatings are obtained by chemical deposition followed by drying.

SILICATE – TITANIA COATINGS

Wollastonite is calcium silicate considered in medicine as a material for artificial bones and dentistry roots. Its advantage is easy formation of HA coating in SBF. In order to increase mechanical properties and secure good biocompatibility the composite coatings were used the mixture of wollastonite and titania in powder form obtained by milling deposited by plasma spraying at atmospheric pressure [75]. Microstructure of such coatings is composed of wollastonite and rutile which do not react during spraying. The advantages of such coatings include good adhesion of coating and a base metal (Ti6Al4V) and relatively good Bond strength, above 30 MPa. The formation of carbonate-containing hydroxyapatite (CHA) is observed on the surface followed by thin layer of silicate if the coating possesses a large amount of silicate (pure wollastonite) or

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composite with above 70% of silicate. Such coating enhances adhesion of osteoblasts, their proliferation, cytocompatibility.

ALUMINIA COATINGS

The deposition of porous alumina ceramics on the Ti alloys was proposed [76]. The interrupted loading at 0.15 Hz of specimen, composed of 15 min long cycles for many days was shown to positively influencing formation of bone proteins.

GLASS - CERAMICS COATINGS

The mostly used bioglasses include: crystalline apatite containing bioglass, wollastonite, diopside and glansy matrix of CaO-P_2O_5-MgO-SiO_2-CaF_2 type. Glassy-ceramic coatings demonstrate very good biocompatibility [6], close to the HA, and very good bonding.
The coatings made of silicate glasses SiO_2-CaO-MgO-Na_2O-K_2O-P_2O_5 on the Ti-6Al-4V alloy by enamel technique reach 50-70 μm in thickness. The coatings with Si content > 55% do not crack, are not subject to delamination, are well adjacent to the base, and with Si content > 60% are more resistant to corrosion. The cracks were observed in SBF which reached the interface and initiated delamination [77].
The heating of CaO-P_2O_5-TiO_2-Na_2O powder at 1073-1125 K gives the coating composed of mainly Ca phosphate □-$Ca_3(PO_4)_2$. Such coating has fatigue strength 15% better than that of the uncoated alloy which can be attributed to creation of hard α+□ layer, with small amounts of ω phase. The coating is perfectly adjacent to the surface of Ti-29Nb-13Ta-4,6Zr alloy in mechanical tests. Ageing at 673 K for 259.2 ks substantially improves the fatigue strength [78].
The properties of zirconia were improved by deposition onto their surfaces of bioactive P-Si glassy ceramics. The coatings 200-300 μm thick were prepared by firing. In in vitro studies during 30 days in SBF, the higher proliferation and expression rate of APF were observed [79].

CARBON AND ORGANIC COATINGS

The classical diamond-like carbon (DLC) coatings are formed of amorphous hydrogenated carbon. After incorporation of some amounts of titanium by radio frequency and magnetron sputtering the TiO_2 and TiC particles may appear inside the coating resulting in enhanced proliferation and redcued activitiy of osteoclast-like cells [80].
Another approach is modification of the surface of Ti-6Al-4V alloy by ion beam melting of deposited layer of carbon [81]. The formed 200 nm coating has an

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approximate composition $Ti_{0,8}O_{0,3}C_{0,2}$. After three months of exposure in SBF the hydrophosphate and dihydrophosphate containing coating is grown.
When the Ti surface is modified by deposition of thin layer from plasma propylene and after addition of 40% acrylic acid, on the surface the atomic bonding of collagen deposited from 0.5 acidic solution appears. The presence of collagen increases osteointegration and biocompatibility of Ti surface [82].
The polimer coating may be also formed from electrochemically deposited polypirole. The polymer is able to modify the surface by biologically active molecules and then to stimulate positive interactions with bone tissue [83].

TITANIA COATINGS

The titania coating can be obtained by sol-gel technique [84]. Its structure is very similar to titanium oxide formed in natural conditions.
In [85] the application of aerosol-gel coatings composed of 1 μm thick titanium oxide was characterized. The hardness of coatings ranged between 15.8-19.5 GPa and Young modulus between 142-168 GPa are increasing heating temperature between 150-800°C. The coatings enhanced the cell growth.
Implantation of amine containing ions on the titanium oxide on titanium, obtained by plasma spraying, enhances adhesion and proliferation of osteoblast cells [86].

ZIRCONIA COATINGS

The ZrO_2 containing 4% CeO_2 and 3% Y_2O_3 was deposited on titanium and CoCrMo steel o [87]. The coatings were rough, porous and remelted.
The biomedical zirconia is very controversial material as concerns its application. It has been applied over than 20 years ago in order to solve the problem of brittleness of alumina and cracking of implants. The number of implantation made with an use of zirconia Hades femoral implants exceeded 600,000 a few years ago [88]. The biomedical zirconia has high mechanical properties resulted from strengthening phase transformation increasing its cracking resistance. The phase transformation relies on change of metastable tetragonal grains into monoclinic phase at the rack tip. The transformation is associated with a volume expansion and increase in compressive stresses. On the other hand, zirconia is subject to susceptible to cracking on the styrene in presence of water. The manufacturers claim that till the catastrophic failure of over 400 femoral head implants made of zirconia in 2001 the problem of cracking has been very limited, the more promising solution could be a composite of alumina and zirconia.

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SUMMARY

The surface engineering is the most promising tool to improve the biocompatibility and to introduce bioactivity of metallic materials [89,90] which still constitute the best technical solution for load-bearing implants. Among various surface engineering techniques, the application of deposited coatings has been confirmed to substantially increase in vitro biochemical properties and in vivo osseointegration rate and bone – implant interface strength.

The variety of coatings, coated materials, deposition technologies and parameters may result in coatings of different crystallinity, thickness, chemical and phase composition, microstructure. Moreover, the coatings must be designed taking into account the application of an implant. Therefore, the optimization of such processes seems very difficult and research studies may only show the features of coatings, development directions, potential applications.

Nowadays, the classical uniform coatings, multiplex coatings and composite coatings are proposed. Among them, the phosphate coatings play very important role. The most popular air and vacuum plasma spraying is criticized because of weaker interface strength, and proposed to change by more sophisticated techniques like electrophoretic precipitation, powder metallurgy, ion beam sputtering, high velocity oxy-fuel (HVOF) combustion spraying, sol-gel technique, biomimetic deposition.

The composite coatings based on HA promise better biochemical and mechanical properties. As the strengthening material, Ti, Ti alloys, titania and zirconia particles, zinc particles, glasses are suggested, and some organic compounds and polymers can be used especially to improve the biochemical behaviour.

Among another coatings, titania, zirconia, aluminia, carbon and organic, glass – ceramics and titania – silicate coatings are mostly proposed.

It seems that the surface engineering is the best way to further improve biochemical properties. Complex investigations of various material combinations and parameters must be performed with an use of approximate modelisation tools, like neural network and fuzzy logic, to optimize the properties of implant systems.

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