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Bioceramic Coatings on Metallic Implants: An Overview

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Abstract

Metallic implants sometimes fail in orthopedic surgeries due to insufficient bio-functionality, implant-associated infections, poor osteointegration due to high inertness (Ti, Co-Cr, stainless steel alloys), and a too fast degradation rate (Mg-based alloys). Bioceramic coatings are among the most appropriate solutions for overcoming these drawbacks. After providing a picture of the history as well as the pros and cons of the different types of metallic implants, this review focuses on bioceramic coatings that can be applied on them, including metal oxides, calcium phosphates, silicates, glasses, glass-ceramics, carbon, etc. Various coating strategies and applications are briefly described and discussed, with emphasis on a selected number of highly promising researches. The major trends and future directions in the development of bioceramic coatings are finally suggested.

Keywords: Bioactive glass; Glass-ceramic; Bioceramic; Metallic implants; Coating; Biomedical applications.

1. Introduction

1.1. Context and significance

Over the last 50 years, thanks to the impressive progress achieved by medical and surgical sciences, the world population has progressively been getting older [1]. However, the elderly may suffer from some typical age-related diseases, such as arthrosis or osteoporosis, which often require replacing dysfunctional hard tissues with artificial devices made of biomaterials able to restore physiological conditions [2]. In the attempt to tackle this challenge, several research groups have focused their attention on tailoring the characteristics of different biomaterials to obtain truly efficient biomedical implants. In the past decades, the gold standard materials in hard tissue applications have been metallic biomaterials, representing around 70-80% of implants produced [1, 3].

From a general viewpoint, the main limitations of inert metallic implants are associated with weak osteointegration, which leads to the development of a fibrous collagenous capsule around the implant causing interfacial displacements, and the release of metal cations into the body, provoking local or systemic toxic effects. On the other hand, degradable implants should have a controllable degradation rate and prolonged mechanical stability [4].

In this regard, the application of a coating – and specifically a bioactive coating – is an effective strategy to improve the overall performance of metallic implants while bringing significant benefits to the patient, including improved stability and longer life of the device by bonding it to the host bone as well as protection of the substrate from corrosion, thereby avoiding the release of potentially toxic metal ions *in vivo* [3, 5]. For example, **Figure 1** shows an *in vivo* implantation of coated metallic implant and some of the associated advantages.

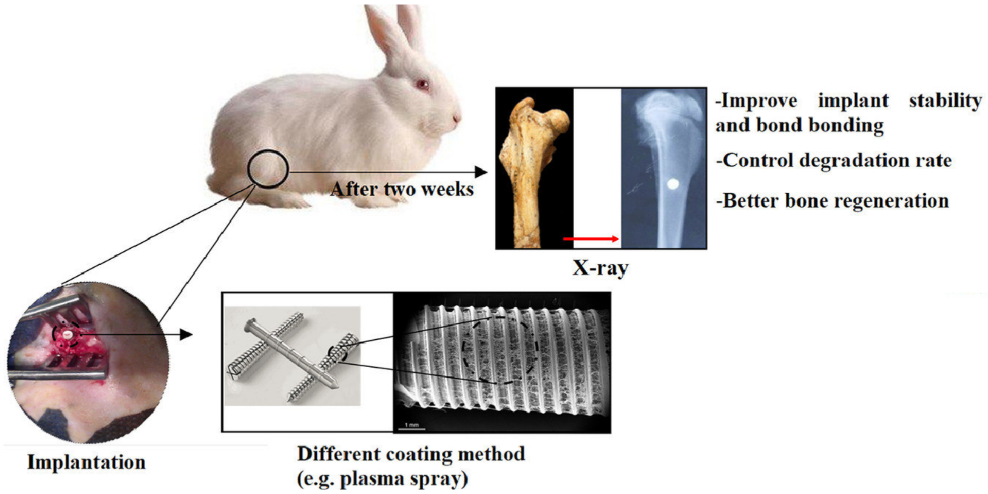

Figure 1. The *in vivo* implantation of a coated metallic implant (*e.g.*, screw) and its beneficial effects [6].

The present paper aims at giving a comprehensive overview of bioceramic coatings, including the inert/bioactive and crystalline/amorphous ones, with focus on their application on metallic implants. The various coating methods as well as the advantages and limitations of the different coating options, in terms of both materials and technologies, proposed in the recent literature are described and discussed, also highlighting the challenges for future research.

For a proper understanding of the subject, a brief introduction to metallic implants is set out below.

1.2. Metallic implants: a short overview

Metallic materials exhibit excellent properties in terms of mechanical strength, elastic modulus, and ductility, which are typically required to achieve optimal long-term support and stability performances *in vivo* for load-bearing implants [3]. The most common metallic materials for medical implants and prostheses include stainless steels, cobalt (Co)-chromium (Cr) alloys, titanium (Ti) and its alloys, and magnesium (Mg) alloys; alloying elements such as molybdenum

(Mo) and zirconium (Zr) can also be added for particular purposes [7, 8]. The choice of the metal is mainly dependent on the functions of the implant and the biological environment. The first metallic implants were produced in the 1920s and were made from stainless steel. Nowadays, the 316L-type stainless steel (SS) is one of the most commonly used alloys for metallic implants ranging from the cardiovascular field to otorhinology [9, 10]. SS-316L was introduced as an evolution of stainless steel 302 to enhance the corrosion resistance in chloride-rich environments like body fluids (**Figure 2**).

Figure 2. Failure of stainless steel implant due to corrosion [11].

Then, 316L composition (**Table 1**) was developed using a small amount of carbon (less than 0.03%) to achieve better corrosion resistance in chloride solution. The main alloying elements in 316L steel are Cr, Ni and Mo [12].

Table 1. Composition of 316L stainless steel [12].

Element		**C**	**Mn**	**P**	**Si**	**Cr**	**Ni**	**Mo**	**Fe**
SS-316L (wt%)	Min	0.002	-	-	-	17	11	2	Balance
	Max	0.03	2	0.05	1	19	14	3	Balance

Indeed, a high amount of Cr reduces environmental corrosion and a higher content of Mo and Ni further increases corrosion resistance in a chloride-rich environment [12].

Although SS-316L composition shows appealing mechanical properties, several studies demonstrated that a high nickel content in stainless steel could elicit toxic effects in the human body. Therefore, research has been addressed to the design of Ni-free stainless alloys [13].

Another important family of metallic implants for hard tissue replacement is represented by cobalt-based alloys, among which CoCrMo and CoNiCrMo are the most commonly used in orthopedic applications [13].

The role of different alloying elements in cobalt alloys is shown in **Table 2**. Cobalt-based materials have been selected because of their high mechanical properties and excellent corrosion resistance [12].

Table 2. Role of different alloying elements in cobalt-based implants [12].

Element	Role in Co-alloy
Cr	Enhancement of wear and corrosion resistance
Ni	Enhancement of corrosion resistance, increase of strength and castability
Mo	Enhancement of corrosion resistance and increase of strength
C	Enhancement of wear resistance and increase of castability
W	Enhancement of strength, but decrease of corrosion fatigue strength and corrosion resistance

Although cobalt, chromium, and nickel are classified as toxic elements, CoCrMo combinations exhibit excellent biocompatibility, showing no – or minimal – adverse effects due to their high corrosion resistance, limiting the ion release of such elements in the body [14, 15].

In summary, the main features of cobalt-based alloys are excellent corrosion and wear resistance, optimal mechanical properties and high fatigue resistance in air, while their main limitations include low ductility, poor fatigue resistance in contact with simulated body fluids and expensive treatments required [11]. Furthermore, CoCrMo alloy showed almost no bioactivity in the physiological environment and poor osteointegration, even lower than stainless steel [16].

After being previously adopted as structural materials in aerospace applications, Ti alloys were used to develop dental and bone implants in the 1950s [11]. Titanium is classified as a non-toxic element even at high doses [17]. While pure titanium can be used in few applications due to insufficient mechanical and fatigue strength, Ti alloys are characterized by higher strength and corrosion resistance in physiological environments compared to other common alloys. For these reasons, Ti alloys are extremely attractive for biomedical applications although being more expensive than other commercial options; moreover, the addition of alloying elements such as Al, V, Nb, Zr and Mo can further increase strength values [18].

Generally speaking, the Ti6Al4V alloy is currently one of the most suitable metallic options in biomedical applications, thanks to its excellent mechanical properties and corrosion resistance [11]. The mechanical strength of this Ti alloy is comparable to that of SS-316L, while the specific strength is superior to that of cortical bone; furthermore, the Young's modulus is very close to that of cortical bone, thus avoiding the problem of stiffness mismatch [19]. On the contrary, the main drawbacks of Ti alloys are associated with the relatively low wear resistance and inferior fatigue/fretting fatigue strength, which may limit their application in long-term load-bearing joints to patients with a not-so-active life [11]. Although titanium alloys are considered bioinert and highly biocompatible, Ti6Al4V can induce toxic effects in the body when corroded and in contact with the bloodstream owing to the release of aluminum and vanadium ions [20].

Biodegradable Mg alloys are also promising candidates for orthopedic and cardiovascular implants and have attracted increasing attention since they carry no need for secondary removal surgery.

They have advantages over traditional metallic materials, ceramics, and biodegradable polymers. The densities of magnesium (1.738 g/cm^3) and magnesium alloys (1.75-1.85 g/cm^3) are very similar to that of human cortical bone (1.75 g/cm^3), while the density of biomedical titanium alloy Ti6Al4V is 4.47 g/cm^3. As regards biocompatibility, magnesium ions are present in a large amount in the human body and are involved in many metabolic reactions and biological mechanisms. The human body usually contains magnesium, approximately 35 g per 70 kg body weight, and the daily demand is about 375 mg [21-24]. Commercial magnesium alloys containing aluminum and zinc (AZ31 and AZ91) and/or rare earth elements (LAE442 and WE43) exhibit excellent mechanical properties. These alloys have already been successfully tested *in vivo*, *e.g.*, as a material for stents, screws, and scaffolds. However, one of the concerns for magnesium in clinical use is hydrogen evolution due to the corrosion process in a physiological environment. Besides, pH increase during Mg dissolution in few days can harm the surrounding host tissues [21-24].

2. Coating methods and functions

The interactions between the biological environment and biomaterials take place on the surface of metals and alloys, and the first biological response from living tissues to these “foreign” implants depends on the surface characteristics [25]. As already mentioned, the fundamental limitation of applying metals and alloys as medical biomaterials is their corrosion performance because of the possible release of toxic metallic ions and particles through corrosion or wear processes [26, 27]. Their potential clinical applications are significantly restricted due to poor corrosion resistance, localized corrosion, and rapid degradation rate *in vivo* [28, 29]. Therefore, the ability to modify the surface characteristics while preserving the bulk properties is essential, and surface modifications addressed to prepare a hard, biocompatible and corrosion-resistant coating have always been an interesting approach in the biomaterials field [30, 31]. Hence, developing appropriate strategies to overcome these limitations has drawn much attention and has been widely deployed in recent years. In this direction, producing protective layers as well as tailoring the composition and microstructure have been considered to improve the corrosion performance of metals and alloys upon contact with body fluids. Besides elemental alloying, depositing surface coatings and conducting surface treatments are, generally, two possible approaches developed to produce protective ceramic, polymeric, and composite layers for enhanced corrosion resistance [28, 32]. Applying surface coatings that act as a physical barrier is a cost-effective, practical, and straightforward way to easily prevent contact between substrates and the corrosive medium. Surface modification and functionalization mainly employ noble coatings to isolate the underlying parts from the aggressive media, while alloying is challenging due to the low solubility of many elements in some metals [33]. The protective characteristics of a coating generally rely on the material stability and ability to slowly wear away, thus allowing controlled degradation of both coating and substrate [30].

In addition to the role of coatings in corrosion protection, various functionalized coatings have been introduced to improve the performance of medical materials since the concept of bio-adaptability covers both biological and material aspects within a certain micro-environment and molecular mechanism [29, 34]. Typical examples of functionalized coatings include smart coatings (*e.g.*, self-cleaning) [34], bio-functionalized coatings (i.e., drug-loaded, antibacterial, biodegradable and biomimetic coatings) [35, 36], super-hydrophobic coatings, and self-healing coatings [37]. Therefore, other functions, including an enhancement of biocompatibility or osteointegration in the case of orthopedic applications, bioactivity, antibiotic/local drug delivery ability, are key added values that biomedical coatings should possess [38].

Diverse classification systems can be adopted to categorize surface coatings according to the coating formation mechanisms, the chemical nature and atomic structure, mechanical, physical, chemical and biological techniques listed in **Table 3**. Commonly conversion coatings and deposited coatings have been known as the two main classes of surface coatings. Conversion coatings as in situ-grown surface coatings are prepared by specific reactions between the environment and base material. Indeed, the metallic substrate surfaces are converted during a chemical or electrochemical process into an oxide layer. The oxide layer grows inwards and outwards simultaneously related to the original metal surface. Therefore, the geometry of the component changes (increment of thickness) and the presence of an interlayer to increase the binding force between the substrate and surface layer can be considered [28]. Deposited coatings, defined as ex-situ coatings, can be obtained by several techniques such as cathodic electrodeposition [39], sol-gel [40], dipping [41], immersion [42] and spraying [43]. Deposited coatings usually serve as a final layer to improve substrate functionality due to the flexibility and multiple compositions of the coatings and weak adhesion based on mechanical bond or electrostatic interaction [29]. Furthermore, coating preparation methods based on various energy sources can be subdivided into electric energy (i.e., micro-arc oxidation (MAO), electrolytic deposition (ED) [44] and layer-by-layer (LBL) assembling) [45], chemical energy (i.e., sol-gel and chemical conversion) [46], and magnetic, thermal and mechanical energy (i.e., friction, physical vapor deposition, and peening) [29]. Among the physical functionalization techniques, the modern laser methods (i.e., pulsed laser deposition (PLD) [47, 48], laser direct-writing (LDW) [49], matrix-assisted pulsed laser evaporation technique (MAPLE) [50], and combinatorial-MAPLE (C-MAPLE) [51]) provide attractive advantages, such as good adhesion of film to substrate, precise control of thickness, coating uniformity, stoichiometric transfer, and experiment reproducibility.

Laser-based methods allow a great spatial control over the regions/points where the coating is applied as well as on the rate and power of irradiation. [52, 53].

It has to be noted that the nature of the coatings produced by each technique can be very different in terms of properties such as internal stress, morphology, hardness and toughness. These differences yield significantly different tribological behaviors. Recently, nanostructured coatings studied for biomedical applications have shown high corrosion resistance and biocompatibility. Anti-corrosive, antibacterial, thermal barrier, anti-abrasion, self-healing, anti-reflection, anti-graffiti, waterproof and non-stick coatings are studied as some examples of nanostructured coatings in medical applications [54-57].

Table 3. Classifications of coating methods on metals and alloys developed for medical applications.

Classification system	**Method**	**Ref.**
Mechanical coatings	Shot peening Friction or attrition	[58, 59] [60, 61]
Physical coatings	Physical vapor deposition Magnetron sputtering Laser cladding Plasma spraying Pulsed laser deposition 3D bioprinting Electron beam deposition Ion implant technologies	[62] [63, 64] [54, 65] [66] [67, 68] [69] [70] [71]
Chemical coatings	Chemical conversion Chemical vapor deposition Anodic oxidation (anodization) Electro-deposition Sol-gel process Electro-less plating Micro-arc oxidation Plasma electrolyte oxidation Layer-by-layer assembly Ionic liquid	[72-74] [75, 76] [77] [78, 79] [42, 80] [81] [82, 83] [84, 85] [86] [87]
Biological methods	Bio-mineralization Molecular recognition	[88, 89] [90, 91]
Coating formation mechanisms	Chemical conversion Deposited coatings	[72, 74] [92-94]
Chemical nature and atomic structure	Metallic coatings Ceramic and inorganic coatings	[64, 95, 96] [97, 98]

	Organic and polymeric coatings Composite coatings	[99, 100] [80, 101]

3. Ceramic coatings

Ceramic coatings are extensively studied to modify the surface of metals or alloys to obtain appropriate corrosion resistance because the chemical nature of metal oxides is more stable than pure metals and metal hydroxides. Ceramic and inorganic coatings are mainly composed of oxides (*e.g.*, Al_2O_3, TiO_2, ZrO_2, SiO_2 and CeO_2), calcium phosphate (CaP) salts, silicates, carbon, layered double hydroxide (LDH) [56]. **Table 4** shows examples of commonly used ceramic coating for medical applications in the human body. Ceramic coatings can be classified into substrate-involving coatings and non-substrate-involving coatings, depending on whether the substrates are involved in the coating formation process or not [58]. More specifically, bioceramic coatings are generally divided into two main classes, bioactive and bioinert coatings. Bioinert ceramic coatings, including zirconia and alumina, have proper biocompatibility and higher mechanical properties than bioactive coatings [102]. The bio-application of bioinert ceramic coatings has mainly been limited by their high elastic modulus and poor interaction ability with the surrounding living tissues [11, 103]. On the contrary, bioactive ceramic coatings, including calcium phosphates and glasses/glass-ceramics, are more widely studied to treat – for example – titanium implants due to their ability to improve the adhesion between the bone and the implant via their biochemical interaction with the body [104].

Table 4. Various bioceramic coatings applied for medical applications in the human body.

Coating material	**Advantages**	**Medical application**	**Ref.**
Metal oxide coatings (TiO_2, Al_2O_3, ZrO_2)	High corrosion resistance High mechanical properties	Dental implants Ophthalmic implants Devices for increasing alveolar area	[105-107]

		Maxillofacial reconstruction	
Calcium phosphate (CaP) coatings	Major mineral component of bones and teeth Promoting normal human cell growth High osseointegration capability	Spinal implants Skull plates Percutaneous devices Maxillofacial reconstruction	[30, 104, 108]
Bioactive glass and glass-ceramic coatings	High osseointegration capability Excellent bioactive behavior Good bonding with the host tissue	Bone tissue applications Dental implants Spinal implants Maxillofacial reconstruction	[109-111]
Silicate-based coatings	Better osteointegration Better radiopacity and bactericidal properties Better cell adhesion and proliferation	Orthopedic implants Skeletal tissue applications Bone tissue applications Bioactive dental cements	[112-118]
Nitrides (TiN, ZrN, NbN, TiAlN) and Oxynitrides (TiON, ZrON, TiSiON) coatings	High corrosion resistance High adhesion on the metallic surfaces Good friction coefficient	Dental implant coatings Metal components of joint endoprostheses Fracture fixation devices	[119-121]
Carbon-based coating (diamond-like carbon (DLC), carbon nanotube (CNT), carboitrides)	Low friction coefficient Low wear rate High biocompatibility with blood	Artificial heart valves Artificial ligaments and tendons Orthopedic fixation devices	[122-125]

3.1. Metal oxide coatings

Several coating techniques have been developed to produce non-substrate-involving metal oxide coatings on metals and alloys, such as the sol-gel process [42, 80], atomic layer deposition (ALD) [126], electrophoretic deposition (EPD) [127], electrodeposition [78, 79], plasma spraying [66], atmospheric plasma jet and magnetron sputtering [63, 64]. Among these methods, sol-gel process, ALD, EPD and spray coating are the most commonly used techniques to fabricate a bio-coating on metals and alloys. Moreover, plasma electrolytic oxidation (PEO), also called micro-arc oxidation (MAO), and anodic oxidation (AO) are the most studied substrate-involving approaches to produce metal oxide coatings [126, 127]. Both techniques use alloys as the anode, and the coatings are mostly composed of metal oxides [30, 55, 128]. The thickness of coatings prepared by both methods is strictly related to the stopped voltage, which is much lower than that of plasma electrolytic oxidation (PEO) [55, 128]. For example, **Figure 3** illustrates an MAO device for coating. A portable pulsing plasma source usually provides a constant voltage. The MAO process is generally performed under a constant frequency and a duty cycle of 4% for 10 minutes. The bath temperature should be controlled [129]. Different metal oxide coatings on metallic biomaterials and their main results are summarized in **Table 5**.

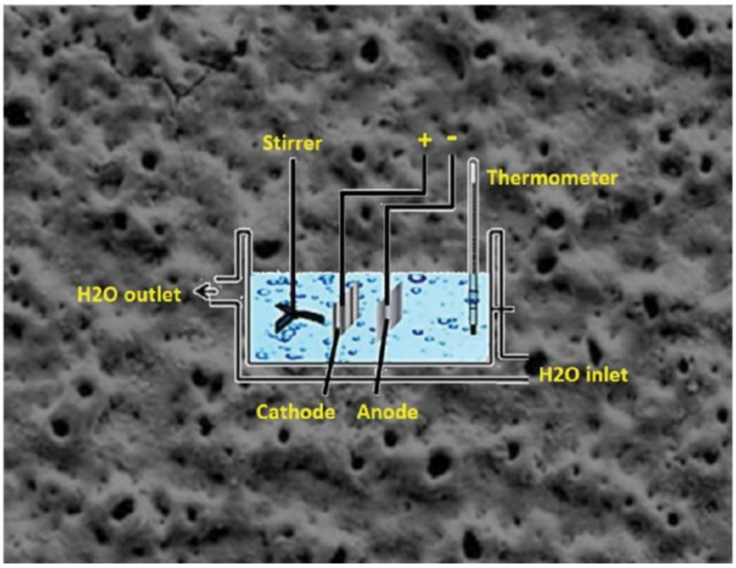

Figure 3. Schemes of the device for micro-arc oxidation. The background shows the microstructure of the ceramic oxide coating [129].

Table 5. Different metal oxide coatings on metallic biomaterials and their main results.

Metal Oxide coatings	**Metallic substrate**	**Coating method**	**Coating thickness (µm)**	**Main results**	**Ref.**
Al_2O_3	NiTi alloy	Micro-arc oxidation	4	Higher corrosion resistance Improvement in suppressing the release of toxic Ni ions	[130]
Al_2O_3	Low alloy steel and	Pulsed magnetron sputtering	-	Coating has a stoichiometric Al_2O_3 composition, and is	[63]

	titanium alloys			extremely dense with no discernible structural features or defects	
Al_2O_3/TiO_2 mono/multi-layers	316L stainless steel / titanium substrates	Atomic layer depositions	0.1	Improvement in corrosion protection TiO_2 monolayer coating showed the highest delamination area Al_2O_3 monolayer showed the smallest delamination areas	[126]
ZrO_2	AZ91D magnesium alloy	Electrophoretic deposition	11-31	Successful barrier layer against corrosive ions even in longer periods of time	[131]
ZrO_2, TiO_2 and TiO_2-ZrO_2 layers	Micro-arc oxidized aluminum alloys (MAO/Al)	UV-assisted sol-gel process	0.98	Improvement in the anti-corrosion ability ZrO_2 pore-sealing layer showed higher anti-corrosion characteristics than other layers UV irradiation could effectively diminish the micro-cracks	[105]
TiO_2	Mg substrate	Liquid phase deposition	2.75-4.15	lower corrosion current with a low rate of in vitro degradation Remarkably suppressing *in vitro* degradation rate	[132]
TiO_2	Mg-Ca alloy	Sol-gel process	-	Improvement in corrosion protection	[133]
TiO_2	Pure Mg	Liquid phase deposition	2	Better corrosion resistance	[134]
TiO_2	AZ31 magnesium alloy	Sol-gel and dip coating	-	Significant enhancement in adhesion Higher cell interaction and attachment	[135]
TiO_2-hardystonite	Mg-Ca-Zn alloy	Electrophoretic deposition/ physical vapor deposition	5-6	Improvement in both corrosion resistance and the cytocompatibility	[136]
TiO_2-Nb_2O_5	Pure Ti	Sol-gel process and dip coating	-	Adding therapeutic effects Suppressing drastic corrosion Good biocompatibility Safe for orthopaedic applications	[107]
TiO_2/alginate	AZ91D Mg alloy	Electrophoretic deposition	9	Better corrosion resistance from 3 to 7 times	[127]
TiO_2/Ag	Grade II CP titanium	Sol-gel process	-	The biocidal effect of the porous coating Improvement in bonding strength	[137]

TiO_2 nanocomposite coatings	Glass slide substrates	Sol-gel process	-	The biocidal effect (E. coli and B. megaterium)	[138]

Recently, Li *et al.* [105] prepared UV-assisted sol-gel ZrO_2, TiO_2 and TiO_2-ZrO_2 layers on micro-arc oxidized aluminum alloys (MAO/Al) and the anti-corrosion ability of the MAO alloys was significantly enhanced. The ZrO_2 pore-sealing layer showed higher anti-corrosion characteristics than those of TiO_2 and TiO_2-ZrO_2 layers. The formation of M-O-M bonds was related to the improvement of anti-corrosion characteristics. It was found that the UV irradiation on the sol-gel coating could effectively diminish the micro-cracks in all of the TiO_2, ZrO_2, and TiO_2-ZrO_2 layers. The cross-sectional SEM images of MAO/Al samples sealed with TiO_2 and ZrO_2 coatings are illustrated in **Figure 4**. The TiO_2 coating thickness was about 980 nm, slightly higher than that of the ZrO_2 coating. Both TiO_2 and ZrO_2 coatings exhibited a dense structure. The compositional analysis by energy dispersive spectroscopy (EDS) of spot T_1 and spot T_2 (Figure 4) showed that the TiO_2 coating was well covered on the MAO layer. According to EDS spectra of spot Z_1 and spot Z_2, a similar phenomenon was achieved for the ZrO_2-sealed MAO/Al sample.

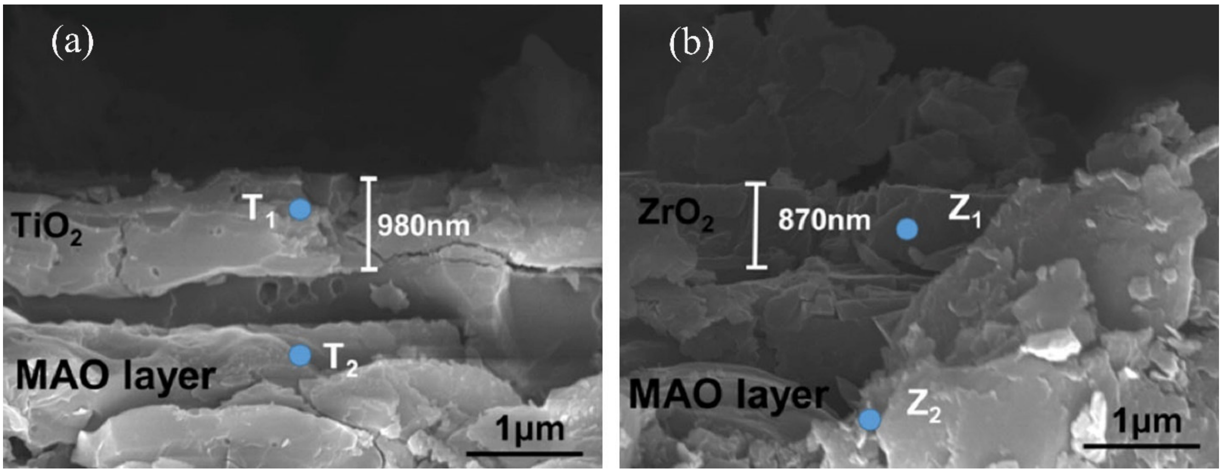

Figure 4. The cross-sectional SEM images of the MAO/Al samples sealed with (a) TiO_2 coating and (b) ZrO_2 coating [105].

TiO_2 coatings are well known to have antibacterial properties as well as strong mechanical properties and biocompatibility. The biomedical applications of TiO_2 coatings include drug delivery systems as well as dental and orthopedic applications [106, 139, 140]. Guo *et al.* [137] observed the biocidal effect of a porous coating containing Ag and TiO_2 nanoparticles obtained by a sol-gel process. Fu and coworkers [138] also observed the biocidal effect of TiO_2 nanocomposite coatings applied on glass slide substrates. Generally, TiO_2 protective coatings have been used on titanium substrates, stainless steel and other metals to separate the underlying parts from the aggressive media [141]. On the other hand, it is difficult to deposit TiO_2 layers onto magnesium alloys because some surface modification techniques provide low adhesion and homogeneity. Nonetheless, several researchers have successfully applied such coatings on magnesium and its alloys [142]. Some of these studies are briefly discussed in the following paragraphs focusing on TiO_2 coatings onto magnesium and its alloys.

Fujita and coworkers used the liquid phase deposition treatment (LPD) method to prepare a corrosion-protective TiO_2 coating on commercially available pure magnesium [134]. Adding an appropriate amount of sucrose to the LPD solution reduced excess homogeneous nucleation of TiO_2 and the formed coating was a double-layer structure. A highly adhesive and thin TiO_2 coating on commercially available pure magnesium without any heat treatment was successfully developed by changing the solution pH with sucrose. Moreover, Marin *et al.* [126] applied four nanometric Al_2O_3 and TiO_2 mono- and multi-layers on polished AISI 316L stainless steel substrates by atomic layer depositions (ALD) method to enhance intrinsic corrosion resistance in aqueous solutions with low concentrations of NaCl. The presence of mono/multi-layers of TiO_2 and Al_2O_3 on the sample surface was confirmed by compositional analysis. TiO_2 mono-layer had the lowest adherence among the different ALD coatings. Cordero-Arias *et al.* [127] produced TiO_2/alginate coating by electrophoretic deposition (EPD) for the first time on AZ91D (Mg alloy).

The coating was deposited without any previous surface pretreatment and the coated alloy showed better corrosion resistance from 3 to 7 times compared to the uncoated alloy.

Chen *et al.* [132] sandwiched a polydopamine (PDA) layer between a TiO_2 coating and Mg substrate to improve the corrosion resistance by deposition in a liquid phase. The coating showed a considerably lower corrosion current with a low rate of *in vitro* degradation in phosphate-buffered saline (PBS). Meanwhile, the mechanical degradation of Mg-Ti composites was studied by Li *et al.* [143], employing the infiltration casting technique. Interestingly, the composite compressive strength was maintained at about 80 MPa, although the Mg wholly dissolved in the composite. On the contrary, Bakhsheshi-Rad *et al.* [136] produced nanostructured hardystonite (HT) and titania (TiO_2)/HT dual-layered coatings deposited on biodegradable Mg-Ca-Zn alloy via electrophoretic deposition (EPD) combined with physical vapor deposition (PVD). Although a single-layer nano-HT coating could reduce the corrosion rate due to the existence of porosities and microcracks, it could not satisfactorily shield the Mg substrate. The corrosion resistance of the nano-HT coating was additionally improved by using a nano-TiO_2 underlayer because it was a uniform, smooth and compact layer with a higher contact angle. Li *et al.* [133] observed that TiO_2 coatings achieved by the sol-gel process significantly enhanced the corrosion resistance of an Mg-Ca alloy in a simulated body fluid (SBF). Tang *et al.* [144] also showed that the coatings improved the corrosion protection and decreased the amount of hydrogen formed by magnesium corrosion. Although hydrogen bubbles are naturally created during the degradation processes, the amount of hydrogen produced can easily be reduced in the presence of the coating as a physical barrier. The improvement achieved by metal oxide coatings on magnesium alloys can also be exploited to increase cellular activity for biomedical applications [106]. Amaravathy *et al.* [135] successfully fabricated a sol-gel TiO_2 coating on magnesium alloy AZ31 via dip-coating technique and showed a significant enhancement in adhesion during biological assessments. Coated Mg showed a higher cell interaction than the unmodified alloy.

Other bioceramics like ZrO_2 and Al_2O_3 have also been used to produce inert coatings to reduce the corrosion rate of metals and alloys. For instance, a corrosion protective Al_2O_3 coating was successfully obtained on the NiTi alloy surface via MAO in an aluminate solution by Xu *et al.* [130] in order to improve the corrosion resistance of the NiTi alloy and suppress the release of toxic Ni ions. The alumina coating exhibited a typical porous surface with low Ni content and an excellent adhesive interface between the substrate and the coating. Besides, the corrosion resistance of the coated NiTi alloy was improved by two orders of magnitude as compared with the uncoated NiTi alloy. Related results also proved that the alumina coating prepared by the MAO method showed great promise for enhancing the biocompatibility of NiTi alloys. In addition, a nano-zirconia coating on AZ91D magnesium alloy for bio-corrosion control purposes was prepared via the EPD method by Amiri *et al.* [131]. The electrochemical results confirmed that the corrosion resistance of the coated alloy was improved effectively and the obtained coating could successfully control the bio-corrosion rate of AZ91D alloy.

In addition to suppressing drastic corrosion of the biodegradable alloys, ceramic oxides are applied on inert metallic alloys to add therapeutic effects. For example, Vanada *et al.* [107] have investigated *in vitro* and *in vivo* pre-clinical safety of two nanoporous mixed metal oxide coatings of TiO_2-Nb_2O_5 (TN) and Sr-HA modified TN (TNS). The TN coating was applied over pure Ti by the combination of sol-gel and dip coating. The additional layer of Sr-HA could trigger bioactivity and positive impacts of Sr on osteogenesis [145]. Biocompatibility evaluations of both implants were carried out by *in vitro* and *in vivo* methods. *In vitro* cytotoxicity showed that both materials were cytocompatible and were proved to be hemocompatible by *in vitro* hemolytic assay. *In* *vivo* bone implantation in rabbits and histopathological analysis further confirmed biocompatibility [107]. The sol-gel process and dipping route permit the coating of complex shapes relatively easily with good control of structure at the molecular level [145-147].

3.2.Calcium phosphate (CaP) coatings

Various calcium phosphate (CaP) phases frequently need different synthesis methods and exhibit different solubility rates, which are dependent on composition, pH, temperature and overall environmental conditions [26, 148, 149]. Several investigations have clarified a distinct difference in the behavior of CaP phases when comparing immersion *in vivo* and *in vitro* media [26, 149, 150]. Biologically relevant CaPs belong to the orthophosphate group and naturally occur in numerous biological structures such as bone and teeth [148, 38]. Bone consists of two main fractions, an inorganic component of biological apatites and an organic component, primarily composed of collagen and water [148]. Synthetic hydroxyapatite (HA) has been confirmed to have very similar characteristics to the naturally occurring CaP of the inorganic component of bone [148, 38]. In summary, CaPs have been utilized as biomimetic (i.e., bone-like) surface coatings to protect metallic substrates against wear corrosion and enhance biocompatibility/bone-bonding ability in orthopedic applications [148, 38, 94]. **Table 6** summarizes the CaP phases used so far to produce coatings in orthopedic applications and their properties.

Table 6. The calcium phosphate (CaP) phases used up to the present time for coatings in orthopedic applications and their properties.

Calcium phosphate phase	Chemical formula	Ca/P ratio	Crystal structure	Biomedical properties	Ref.
Hydroxyapatite (HA)	$Ca_{10}(PO_4)_6(OH)_2$	1.67	Hexagonal	- The naturally occurring mineral form of calcium apatites - Major mineral component of bones and teeth	[30, 55, 94]

				- Improving adhesion, proliferation and differentiation - Promoting normal human cell growth - Induction of no/very limited inflammatory reaction - Non-resorbable (unless produced in nano-sized form)	
Fluorapatite (FA)	$Ca_{10}(PO_4)_6F_2$	1.67	Hexagonal	- Antibacterial activity - Increasing the biocompatibility and bioactivity of biomaterials	[151, 152]
Tricalcium phosphate (TCP)	$Ca_3(PO_4)_2$	1.5	Monoclinic (α-TCP) Rhombohedral (β-TCP or whitlockite)	- Greater solubility than HA/FA ($\alpha > \beta > HA$) - Increasing biocompatibility - Decreasing bone loss	[153]
Octacalcium phosphate (OCP)	$Ca_8H_2(PO_4)_6.5H_2O$	1.33	Triclinic	- Requiring an intermediary phase - Most stable at a physiological pH and temperature - Decreasing inflammatory reactions	[154]
Anhydrous calcium phosphate (monetite, ADCP)	$CaHPO_4$	1.0	Triclinic	- Slightly soluble - Increasing the amounts of Ca and phosphate ions over a set time - Promoting osseointegration and osteogenesis	[94, 155]
Calcium phosphate dihydrate (brushite, DCP)	$CaHPO_4 \cdot 2H_2O$	1.0	Monoclinic	- Increasing the amounts of Ca and phosphate ions - Promoting increased osteointegration	[104, 108]

The most potentially-suitable methods to deposit HA coatings on metallic implants and clinical devices are classified into four major categories: electrodeposition (ED) techniques, wet methods, spray techniques, and laser techniques [55, 104]. Some examples of these coating techniques and their advantages and disadvantages are summarized in **Table 7**. Liu *et al.* [156] deposited dense, firmly adhesive HA thin films on rough 316L stainless steel substrates using a novel water-based sol-gel method. Stoch *et al.* [157] also produced HA films on titanium and its Ti6Al4V alloy by sol-gel technique to facilitate and shorten the processes towards osteointegration. As an inexpensive and low processing temperature process, the sol-gel method produces pure and very thin HA coating (<1 μm) on flat and complex shapes. However, a controlled atmosphere is still required in some stages, and poor adhesion to the substrate was observed [156].

Table 7. Major techniques to produce HA coatings along with their advantages and disadvantages.

Coating methods	Examples	Advantages	Disadvantages	Ref.
Electrodeposition (ED) methods	Electrochemical method Electrophoretic deposition	Simplicity Cost-effectiveness Improvement in corrosion resistance, bonding strength, bioactivity, and biocompatibility	More porous coatings Less adherent coatings	[29, 55, 158, 159]
Wet methods	Chemical precipitation method Sol-gel process Dip coating Spin coating Hydrolysis method Solvothermal method Sonochemical method Hydrolysis method Multiple emulsion method Biomimetic deposition method	Improvement in corrosion resistance Excellent adhesion strength between substrate and coating layer Applicability to complex coating geometry Good homogeneity Lower calcination temperature High phase purity	Difficulty in maintaining a uniform coating thickness Coatings are mostly porous with cracks due to quick evaporation of the solvent and residual water	[55, 156, 157, 159, 160]
Spray techniques	Air spray coating Thermal spray coating Cold spray coating Spray-pyrolysis technique Plasma spraying	Improvement in corrosion resistance Set-up simplicity Cost effectiveness	Not appropriate for precious coating layer	[55, 158, 159, 161, 162]
Laser techniques	Pulsed laser deposition Matrix-assisted pulsed laser evaporation Combinatorial matrix-assisted pulsed laser evaporation	Superior advantages for the fabrication of complex geometry materials Fast deposition time,	The stress concentration cracking around the coating Pinholes, and poor corrosion resistance	[55, 163-167]

		Maintenance of stoichiometry Higher flexibility The ease of growing multilayered coatings		

Plasma spraying is a rapid deposition method to prepare HA coatings (<20 μm) with a lower possibility of coating degradation. Hung *et al.* [168] obtained a desirable combination of biocompatibility and mechanical characteristics for dental implants by properly setting the process parameters for plasma-sprayed HA coating on titanium alloy (Ti6Al4V) surfaces. The HA coating was closely uniform with a thickness of 47–130 μm. Mohseni *et al.* [159] reported a comparative investigation on the adhesion of HA coating on Ti6Al4V implants to analyze nine methods applied for depositing HA onto Ti6Al4V alloys. They reviewed nine techniques, including plasma-sprayed deposition, hot isostatic pressing, thermal spray, dip coating, pulsed laser deposition, electrophoretic deposition, sol-gel process, ion beam assisted deposition, and sputtering. The best adhesion of HA coating to the substrate was achieved by the sputtering technique, while the worse bonding strength was obtained by pulsed laser deposition. Using an interfacial layer (such as TiO_2 or TiN) as the initial coating layer on the substrate followed by the HA coating layer could enhance the bonding strength in all techniques [159].

The *in vivo* response to freeform fabricated cobalt-chromium (CoCr) implants with and without HA plasma-sprayed coatings was also evaluated by Grandfield *et al.* [169]. Specifically, differences in terms of bone contact and bone growth induction were investigated. Transmission electron microscopy (TEM) investigations and histomorphometry showed a considerably higher bone contact on HA-coated implants than native CoCr implants. TEM images revealed an intimate interaction at the HA-bone interface, which is illustrated in **Figure 5**. The existence of a jagged outermost part of the coating in the dark field electron micrograph indicates the integration of the

HA coating with the bone. A separation or crack was observed in the bone rather than at the interface, indicating a strong adhesion-like chemical bonding at the HA–bone interface. Appropriate dissolution resistance, good adhesion, high bioactivity and biocompatibility are benefits of plasma spraying. On the contrary, high processing temperature causes the decomposition of HA and phase transformation of the substrate. Non-uniform coating density is a disadvantage of the plasma spraying method [168-170]. Nevertheless, plasma spraying is currently the only method commercially accepted by the Food and Drug Administration (FDA) for biomedical coatings on dental implants [171].

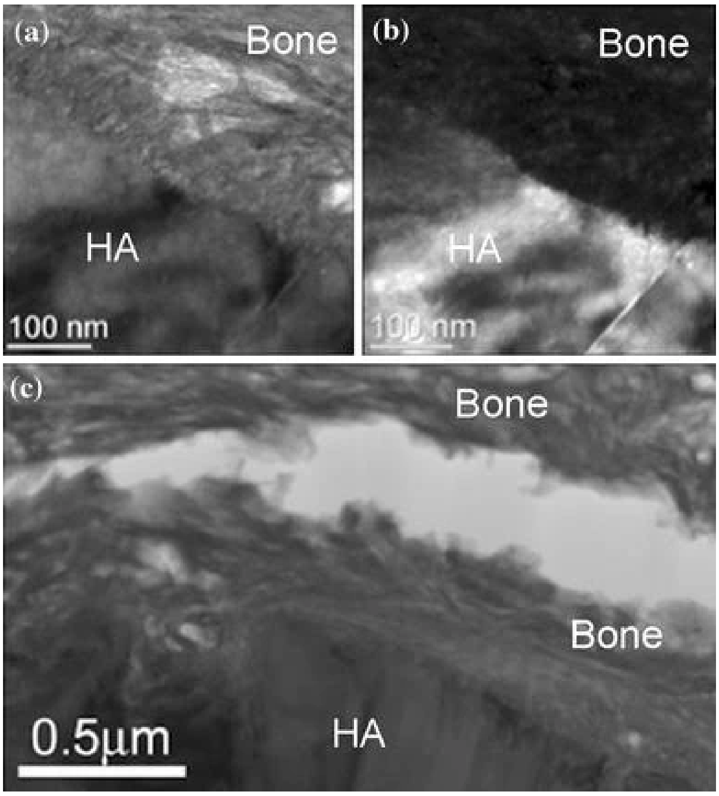

Figure 5. TEM (a) bright-field and (b) dark-field micrographs of the HA–bone interface. (c) Low magnification TEM image of a crack in the bone rather than at the interface [132].

The physical and biological properties of HA coatings obtained by electrophoretic deposition (EPD) were improved by Rad *et al.* [172]. For the first time, they used the EPD process at dynamic voltage to control and improve the physical and biological performance of HA coatings. The results demonstrated that the best adhesions for the coatings are obtained at lower currents of 0.07 and 0.15 mA [172]. Rojaee *et al.* [173] produced fluoridated HA nano-powders with different degrees of fluoridation on micro-arc oxidized AZ91 magnesium alloy by EPD. The main advantages of this approach, such as the ability to apply the coating on complex shapes, obtaining uniform coating thickness (100-2000 μm) and high deposition rate, were pointed out. The main disadvantages of using EPD are the need to apply post-EPD high-temperature thermal treatment for coating consolidation and the challenge in preparing crack-free coatings [104, 172, 173]. Furthermore, Qiu *et al.* [174] studied the corrosion behavior of HA/zirconia composite films on NiTi prepared by electrochemical deposition. Results revealed that the morphology of HA changed from thin flake-flower-like crystals to needle-flower-like crystals when ZrO_2 was incorporated into the electrolyte (**Figure 6**), and the coating was denser. ZrO_2 addition could improve the bonding strength between the coating and the substrate. The corrosion resistance of NiTi was considerably improved almost 60 times after electrodeposition of the HA/zirconia composite [174].

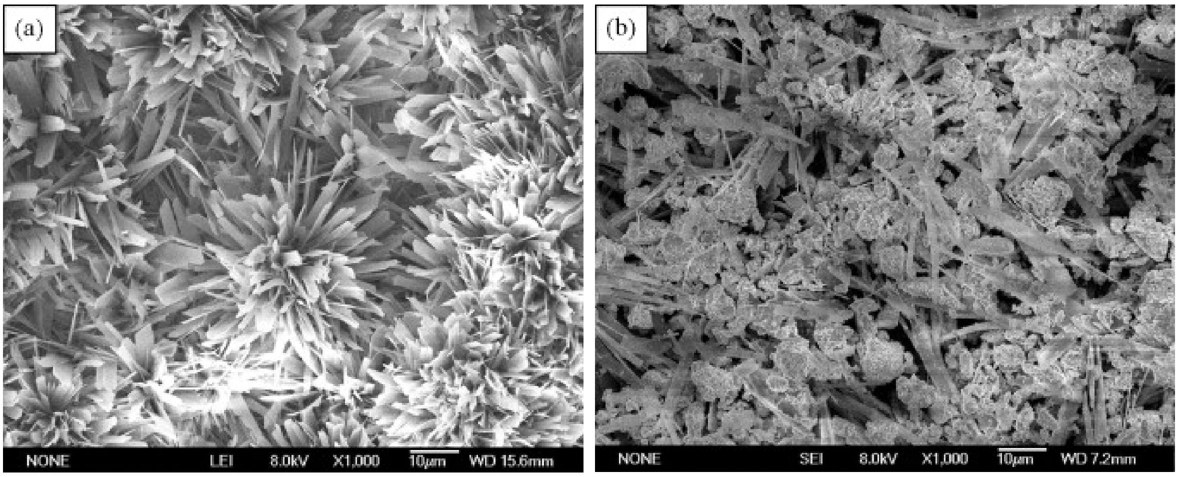

Figure 6. SEM morphologies of the coatings: (a) HA coating and (b) HA/ZrO_2 coating [174].

Wang *et al.* [175] prepared HA coating on CoCrMo implant by an effective electrochemically-assisted deposition pretreatment. It was found that the electrochemical deposition process was a relatively inexpensive method and allowed achieving fast deposition and producing uniform coating thickness (50-500 μm) on complex shapes. However, poor adhesion quality between coating and substrate is an important disadvantage of this method [104, 174, 175]. Bigi *et al.* [176] obtained a rapid biomimetic deposition of nanocrystalline HA coatings on Ti6Al4V substrates using a slightly supersaturated Ca/P solution. A low degree of crystallinity was achieved by the biomimetic coating method. Coating complex shapes, low processing temperature, and preparing bone-like apatite are the main advantages of this coating method [176-178]. Interested readers are encouraged to refer to several good reviews on this topic [53, 179-182]. These overviews illustrate that calcium phosphates, HA coatings, and functionalized compositions significantly improve osseointegration and are viable options in treating an osteoporotic fracture.

Despite their gross similarity, biological bone apatite and stoichiometric apatite show some important differences from several viewpoints. Firstly, in terms of composition, bone apatite is a nonstoichiometric, multi-substituted poorly-crystalline apatite, containing significant amounts of foreign ions with high biological relevance [183, 179]. Each substitution can alter crystallinity degree and lattice parameters of calcium phosphates which have a remarkable impact on solubility and ion release in the biological medium [184, 185]. In addition, some of these ions play a significant biological role, directly influencing host cell response or exerting a therapeutic role. Therefore, the importance of the presence and amount of such ions in ion-substituted calcium phosphates and HAs is undeniable for mimicking the real composition of bone to improve the biological performances of the implant [179]. Cationic and anionic incorporations in the HA lattice are very common in biological apatites, the most diffused being CO_3^{2-} for OH^- (A-type substitution) or for PO_4^{3-} (B-type substitution), and Cl^- and F^- for OH^- [186]. Besides these ions, Mg, Sr, Zn and Mn substitutions for calcium and silicates for phosphates can be detected in human mineralized tissues [185, 187]. A large number of studies have been reported to evaluate the performance of substituted CaP coatings from various points of view [183, 179].

Wet deposition methods are, by far, the most studied techniques to prepare ion-substituted CaP and HA coatings, due to the possibility to simply incorporate significant ions during a wet chemical synthesis strategy, the possibility to cover complex shaped morphologies and the reasonably low costs. However, wet methods are poorly reproducible and hardly industrially feasible [185, 179]. Novel plasma-assisted methods have been emerging, allowing thin coating to be deposited with superior adhesion to the metallic substrate and reduced tendency to crack [185, 179]. Compared to wet deposition techniques, plasma-assisted methods allow for much faster coating of the surface, which is a significant benefit from an industrial point of view [185]. Compared to plasma spraying (PS), novel plasma-assisted methods allow for an easier transfer of the target composition and morphology with lower porosity and lower tendency to cracking and delamination [188]. Among plasma-assisted techniques, radio-frequency magnetron sputtering (RF-MS) [165, 189] and pulsed laser deposition (PLD) [165, 190] are the most used in the biomedical domain for manufacturing thin coatings on bone implants. Various ion-substituted octacalcium phosphate (OCP) and HA coatings, such as carbonated hydroxyapatite (CHA), Mg-HA, Mg-OCP, Sr-HA, Sr-CHA, Si-HA, Mn-CHA and Mn-OCP, have been deposited by PLD method [163, 164]. Matrix-assisted pulsed laser evaporation (MAPLE) [165, 166] and pulsed electron deposition (PED) [191, 192] are emerging methods, allowing a fine control over coating stoichiometry and composition and are gaining increasing attention. Deposition of Sr-HA coatings by PED [193] and combinatorial matrix-assisted pulsed laser evaporation (C-MAPLE) [166, 167] for variable Sr content has been recently reported, too.

3.3. Bioactive glass and glass-ceramic coatings

Metallic implants *per se* have the ability to establish only a mechanical interlocking with the host tissue through morphological fixation [194]; this tendency can be further emphasized by surface roughening. On the contrary, bioactive glasses (BGs) can form a strong bond with the native tissue triggering a cascade of chemical and biological responses, deeply explained by the bioactivity theory of Prof. Hench, thus leading to the formation of a stable interface between the implant and the host tissue [195-199]. Even if BGs may represent ideal osteoinductive and bioresorbable materials for bone tissue engineering applications, their use in load-bearing conditions is strongly limited due to their poor mechanical properties. For this reason, the application of a BG coating may constitute an effective strategy to both enhance osteo-integrative properties of metallic implants and somehow overcome the intrinsic brittleness of BGs [5, 200, 201]. It is also worth underlining that BG coatings can actively stimulate osteointegration, while other bioceramic coatings, such as HA, are only osteoconductive [202]. Different glass compositions, coating-substrate type and properties of main bioactive glass coatings are summarized in **Table 8.**

Table 8. Glass composition, coating-substrate type and properties of main bioactive glass coatings.

Glass system /composition	**Type of coating**	**Type of substrate/implant**	**Properties and function of the coating**	**Ref.**
$52SiO_2$-$30.5CaO$-$9.8Na_2O$-$6.2P_2O_5$-$1.5CaF_2$ (mol%)	Bioactive glass coating	Ti6Al4V dental implants	Stable glass-metal interface	[109]
P_2O_5-Na_2O-CaO-SiO_2 systems	Bioactive glass-ceramic coatings	Titanium dental implants	Nanostructured coating successfully synthesized with good *in vitro* bioactivity	[203]
P_2O_5-Na_2O-CaO-SiO_2 systems	Bioactive glass-ceramic coatings	Titanium implants	Coating crystallinity influenced by processing method parameters Good *in vitro* bioactivity	[110]

45 SiO_2- 6 P_2O_5- 24.5 Na_2O- 24.5 CaO (wt.%) - 45S5 Bioglass®	Bioactive glass coatings	AISI 304 steel substrates	Homogenous microstructure High roughness and porous coating coating Good *in vitro* bioactivity	[204]
49.13 SiO_2-43.19 CaO- 7.68 MgO (wt.%)	Bioactive glass-ceramic coatings	Ti6Al4V implants	Less micro-cracks in coating Bonding strength double of HA coatings Osteogenic and osteoinductive properties Excellent bioactivity	[111, 205]
45 SiO_2- 6 P_2O_5- 24.5 Na_2O- 24.5 CaO (wt.%) - 45S5 Bioglass®	Bioactive glass coatings	Ti6Al4V implants	Osteogenic and osteoinductive properties Excellent bioactivity	[206]
(46-53)SiO_2-(9-20)CaO-(7-24)Na_2O-(0.1-2)MgO-(4-8)P_2O_5-(2-8)K_2O-(0.1-2)Al_2O_3 (mol.%) - Biovetro®	Bioactive glass coatings	Titanium-based implants	80 μm thickness Decreased osteointegration rate Excellent clinical outcomes in clinical trials	[207]

One of the most critical factors for the fabrication of BG coatings is the thermal expansion coefficient (TEC) of such materials. For example, the well-known commercial 45S5 Bioglass® ($45SiO_2$-$24.5CaO$-$24.5Na_2O$-$6P_2O_5$ wt%) has a TEC value ($15 \times 10^{-6}\ ^{\circ}C^{-1}$) significantly higher than that of titanium alloys (about $9 \times 10^{-6}\ ^{\circ}C^{-1}$) [5]. Ideally, the thermal expansion coefficient of the glass should perfectly match with that of the metallic substrate to avoid the glass pulling away from the implant upon processing [200]. In this regard, several scientists have focused their attention on developing different glass compositions with more suitable TEC for application as coatings. It has been demonstrated that the partial substitution of Na_2O with K_2O and CaO with MgO may represent an effective strategy to obtain a tailored design of TEC [208]. Other studies have also addressed the impact of B_2O_3 addition on TEC, demonstrating that, although borosilicate glasses are characterized by a higher dissolution rate than silicate glasses in an aqueous environment, they exhibit lower TEC values [209]. The adhesion between the BG coating and the metallic implant can be evaluated through scratch tests, usually followed by morphological analysis by optical microscopy or SEM, tensile (pull-out) tests or nanoindentation tests [210].

BG and glass-ceramic coatings on metallic implants can be produced by enameling, thermal spraying, radiofrequency magnetron sputtering (RF-MS) deposition, pulsed laser deposition (PLD), sol-gel coating and electrophoretic deposition (EPD) starting from glass micro- or nanoparticles [211]. As mentioned above, a post-deposition high-temperature treatment is usually required to consolidate the coating that undergoes sintering and often simultaneous crystallization, thus being converted to a glass-ceramic material. Polymer/glass composite coatings deposited by EPD do not need this additional processing step as the organic phase acts as a “glue” on the metallic substrate [212, 213].

The use of glass/glass-ceramic coatings on metallic implants has not achieved yet a full translation into clinical practice mainly due to some issues, including TEC-related interfacial delamination and coating stability in the long term (BGs tend to undergo progressive dissolution over time, thus leading to implant failure); however, many efforts have been made by several research groups to develop glass/glass-ceramic materials for this application [202, 209].

The first quantitative assessment about the adhesion strength of BG coatings was carried out in 2000 by Schrooten and Helsen [109]. Melt-derived 52S glass coatings ($52SiO_2$-30.5CaO-9.8Na_2O-6.2P_2O_5-1.5CaF_2 mol%) were applied onto Ti6Al4V dental implants through the plasma spraying method, and then adhesion tests were conducted on the implants after two months of immersion in SBF. The results showed that, although a decrease of 10% in the adhesion strength was recorded post-immersion, the glass-metal interface still remained completely intact [109].

Xiao *et al.* [203] also produced bioactive silicate glass-ceramic coatings on titanium substrates through plasma spraying. In this case, the analysis of the coatings revealed the presence of amorphous and crystalline phases in the coating with different morphological structures (**Figure 7**). In another study, the same authors compared BG coatings with analogous composition but realized by sol-gel and solid precursor plasma spraying methods [110]. The crystallinity of the coating was influenced by the processing method used and its parameters: specifically, the sol-derived coating exhibited a higher crystallinity while the structure of the plasma-derived layer was impacted by several factors, such as liquid precursor feed rate. Plasma spraying was also applied by Lopez Calvo *et al.* [204] to fabricate 45S5 Bioglass® coatings on AISI 304 steel substrates.

In 2014, a new glass-ceramic formulation named M2 (43.19CaO- 7.68 MgO-49.13 SiO_2 wt.%) was used to coat Ti6Al4V implants through atmospheric plasma spray [205].

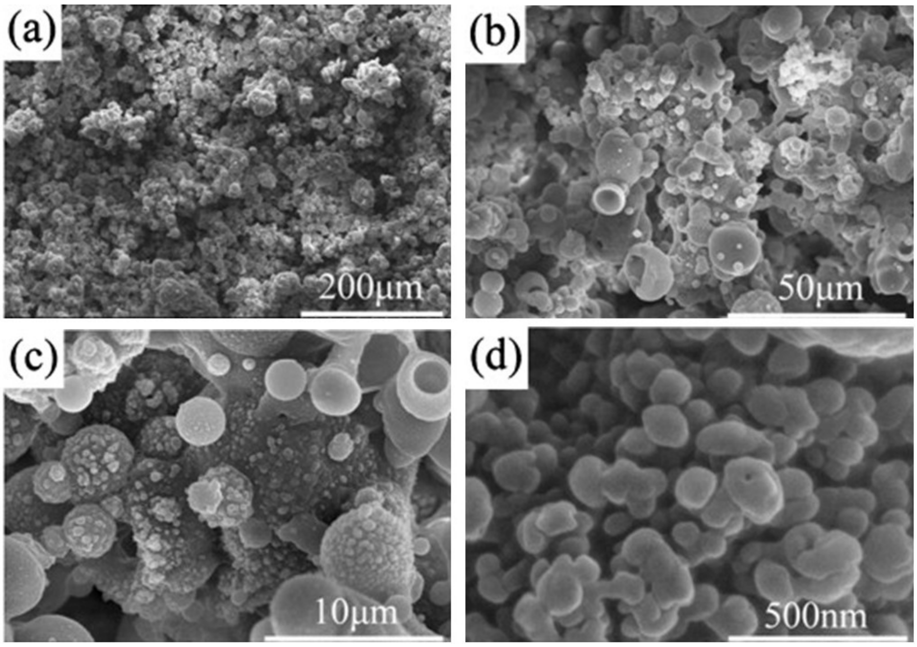

Figure 7. Top surface of bioactive glass-ceramic coatings produced by plasma spraying at different magnifications [203].

These samples were compared to commercial plasma-sprayed HA coatings. The evaluation of the bonding strength reported a value of 35.43 MPa in M2 coating, nearly double the value for HA coatings. M2 coatings were also tested *in vitro,* demonstrating excellent bioactive behavior.

Based on this previous study [205], the same research group has recently experimented M2-coated Ti6Al4V *in vivo* tests on rabbits and HA coating/Ti6Al4V were used as control [111]. Both samples exhibited good bonding with the host tissue, formation of new bone tissue and no foreign body reaction occurred. The histological analysis confirmed the better osteogenic and osteoinductive properties and a better osteointegration with the host bone of M2 coatings (**Figure 8a)** compared to HA samples (**Figure 8b**).

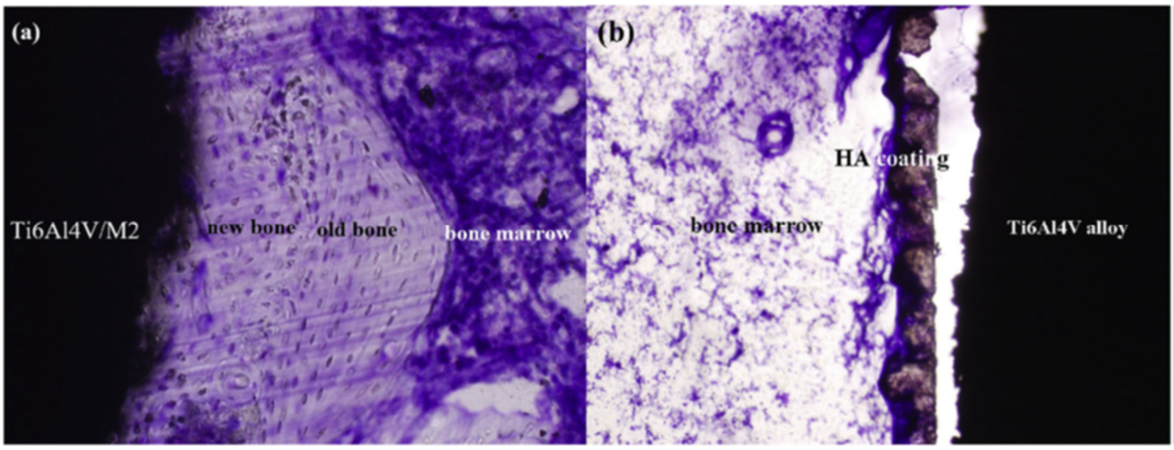

Figure 8. Osteogenesis induced by M2 and HA coatings on Ti6Al4V during *in vivo* tests conducted in rabbits. (a) M2 coating; (b) HA coating [111].

In 2012, other animal tests were conducted by Drnovšek *et al.* [206], who implanted Ti6Al4V porous cylinders coated with 45S5 Bioglass® in tibia holes of ten white rabbits. Analogous cylindrical implants without the glass coating were also inserted as the control system. After ten weeks *in vivo*, the bioactive coating was reabsorbed entirely. Compared to uncoated implants that exhibited only 22% of pores filled, almost a double value (38%) of the porous titanium layer were filled with new bone tissue. This confirmed the important role of bioactive coatings in stimulating osteointegration and osteogenic processes [206].

Alonso-Barrio and his research group performed clinical trials on BG coatings [207] who implanted titanium-based femur stems coated with a layer of Biovetro® (compositional ranges: (46-53)SiO_2-(9-20)CaO-(7-24)Na_2O-(0.1-2)MgO-(4-8)P_2O_5-(2-8)K_2O-(0.1-2)Al_2O_3 mol%), with a thickness of 80 μm, into 70 human patients. The results showed that, after 8 years of follow-up, the survival rate of those stems was 91,4%. Comprehensive clinical evaluations about these trials were carried out considering several key aspects in patient life during the post-operative phase, such as morbidity statistics, pain manifestations, and gait analyses. From these observations, more than three-fourth (77%) of patients were associated with good/excellent outcomes. It has to be mentioned that, unlike the expectations, Biovetro® coating decreased the osteointegration rate compared to plasma-sprayed HA coatings; the reason behind it is still unclear and such an issue deserves further investigation.

In summary, current experimental evidence suggests that the major limitations of BG/glass-ceramic coatings are induced by their inherent bioresorbable behavior. As previously explained, BGs are characterized by various dissolution rates which are mainly influenced by the glass composition/structure (*e.g.*, presence of nanopores increasing the specific surface area) and pH of the environment. The high bioactivity and progressive degradation may cause instability in the implant site which can explain why non-resorbable HA or other bioceramic coatings have been preferred by surgeons for a long time [214]. However, there are still few studies reporting data about the long-term stability of bioactive coatings on metal implants under physiological conditions, especially in humans [207]. Indeed, it is expected that the increasing need for biomedical implants able to meet the requirements of bone tissue engineering and regenerative medicine will boost research in the field of BG and glass-ceramic coatings over the next years, as recently observed for other kinds of BG-based biomedical products [5, 215-218].

3.4. Silicate-based ceramic coatings

Mohammadi *et al.* have recently thoroughly reviewed the recent development and progress of coating metallic implants with silicate-based crystalline ceramics to enhance osteointegration and biocompatibility [6]. The silicate ceramics used for coating purposes include akermanite ($Ca_2MgSi_2O_7$), diopside ($CaMgSi_2O_6$), bredigite ($Ca_7MgSi_4O_{16}$), merwinite ($Ca_3MgSi_2O_8$), monticellite ($CaMgSiO_4$), hardystonite ($Ca_2ZnSi_2O_7$), baghdadite ($Ca_3ZrSi_2O_9$), sphene ($CaTiSiO_5$). **Table 9** summarizes the different coating methods of various silicate-based ceramic coatings on metallic biomaterials. They are primarily used to coat Ti and Mg alloys and stainless steel. A bonding strength and surface roughness ranging from 10-50 MPa and 1.5-12 µm have been also reported [112-118]. Sr-doped silicate coatings have shown better osteointegration properties and doping with Ti/Zr and Zn improve the radiopacity and bactericidal properties, respectively. For example, Hu *et al.* substituted Mg^{2+}, Zn^{2+} and Sr^{2+} ions for Ca^{2+} in plasma-sprayed calcium silicate ($Ca_2MgSi_2O_7$, $Ca_2ZnSi_2O_7$ and Sr-$CaSiO_3$) coatings [118]. They reported that this doping hinders excessive degradation in the physiological environment and, more significantly, improves the biological properties. Their results showed that cell adhesion and proliferation increased the most on the surface of Mg-modified coating. Gene expressions of early osteoblast differentiation markers (COL-I and ALP mRNA) were improved on Zn-modified coating. Gene expressions of later markers for osteoblast differentiation (OPN and OC mRNA) and mineralized nodules formation were accelerated on the surface of Sr-modified coating. Since Mg^{2+}, Zn^{2+} and Sr^{2+} play a regulatory role in different stages of osteogenesis, it was interesting to utilize this approach in developing new coating materials for the orthopedic application. In summary, silicate-based coatings could increase surface roughness and bonding strength and control the degradation rate. It was demonstrated that the combination of a metallic implant with silicate-based coating could result in bactericidal, corrosion-resistive, and bone-implant bonding effects [118]. The addition of Zn in the hardystonite ($Ca_2ZnSi_2O_7$) structure has triggered a potential antibacterial property. Ti6Al4 V substrates coated with this material could significantly suppress the activity of *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*) bacteria [219]. Positively-charged ions (*e.g.*, Ag^{+}, Zn^{2+}) and compounds can attach to the bacterial cell wall and disrupts its membrane and DNA structure [220, 221]. Zinc has also been incorporated into baghdadite ($Ca_7MgSi_4O_{16}$) to turn it into an antibacterial coating. A coating of ZnO/baghdadite on Mg alloys showed a high antibacterial effect [222]. Metallic substrates coated with the nature-inspired biomimetic structure of ion-doped silicate-based ceramics are promising in developing an advanced and robust coating that can significantly improve the coating properties. For example, Jia *et al.* [223] could develop a triple-bioinspired burying/cross-linking interfacial co-assembled coating in which surface functionalized, aqueous dispersed Ag-doped baghdadite ($Ca_3ZrSi_2O_9$) particles were buried within a substrate-anchored organic matrix of polyelectrolyte multilayers (i.e., (poly(ether imide) (PEI)/poly(sodium-p-styrenesulfonate) (PSS))$_n$) through a novel inorganic-organic hybrid layer-by-layer (LBL) co-assembly scheme inspired by mussel (oyster) adhesive and cohesive chemistries. Intimate substrate contacts and well-defined inorganic-organic interfaces were reported, together with good structural and chemical stability, especially after cross-linking. Sustained bioactive ion releasing and appreciable biomineralization activity was also reported *in vitro* [223].

Table 9. Different coating methods of various silicate-based ceramic coatings on metallic biomaterials.

Silicate-based coatings	**Metallic substrate**	**Coating method**	**Main results**	**Ref.**
Akermanite ($Ca_2MgSi_2O_7$)	Ti-6Al-4V	Plasma spraying	High bonding strength to titanium alloy implants High *in vitro* bioactivity Excellent apatite mineralization ability High proliferation rate of rabbit bone marrow mesenchymal stem cellson on akermanite coatings Excellent candidate for orthopedic and dental applications	[224]
	Ti substrate	Pulsed laser deposition	Excellent bioactivity Good effect on stem-type cells Excellent mechanical properties Suitable for the development of medical implants	[225]
	Ti-6Al-4V	Sol-gel process	Uniform and crack-free coating structure Improvement in cell-proliferation rate Promoting cell interaction with bone implants Promising an improved tissue response	[226]

	AZ91 Mg alloy	Electrophoretic deposition	Better corrosion resistance of biodegradable Mg alloy Higher mechanical stability of biodegradable Mg Improvement in the cytocompatibility of biodegradable Mg alloy Promising material to be used as biodegradable bone implants for orthopedic applications	[227]
	AZ91 Mg alloy	Electrophoretic deposition and plasma electrolytic oxidation	Noticeable biocompatibility improvement Slower implant weight loss Reduction in Mg ion released from the coated samples in the blood plasma Lower release of hydrogen bubbles Increase in the amount of bone formation Lower bone inflammation after the surgery	[228]
	Ti-6Al-4V	Plasma spraying	Increase in the level of cell adhesion and proliferation Better cell attachment	[118]
Diopside ($CaMgSi_2O_6$)	Ti-6Al-4V	Plasma spraying	High bond strength of the coating Good Young's moduli Good candidate for bone and dental implants	[112]
	AZ91 Mg alloy	Micro-arc oxidation and electrophoretic deposition	Increase in the corrosion resistance of Mg alloy. Improvement in the in vitro bioactivity of Mg alloy	[229]
	316 L SS	Dip coating	Improvement in the substrate’s bioactivity via an ion-exchange reaction mechanism in vitro	[230]
	AZ91 Mg alloy	Micro-arc oxidation and electrophoretic deposition	Diopside coating slows down the corrosion rate Improvement in the in vitro bioactivity, mechanical stability and cytocompatibility	[231]
	Ti-6Al-4V	Plasma spraying	Good biocompatibility with human osteoblast High bond strength Ability to bond directly to the bone Good candidate for bone and dental implants.	[232]
	Ti-6Al-4V	Plasma spraying	Excellent apatite-mineralization ability	[233]

Bredigite ($Ca_7MgSi_4O_{16}$)			High proliferation level of bone marrow stem cells Improvement in the cytocompatibility	
	AZ91 Mg alloy	Anodic spark deposition and electrophoretic deposition	Improvement in the degradation resistance, bioactivity, mechanical integrity and cytocompatibility of biodegradable Mg alloy Bredigite coatings can delay the corrosion process and improve the mechanical stability and cytocompatibility of the AZ91 Mg alloy in the early stages of bone healing	[234]
	AZ91 Mg alloy	Micro-arc oxidation and electrophoretic deposition	Improvement in the in vitro bioactivity of magnesium alloy Higher corrosion resistance of Mg alloy	[235]
merwinite ($Ca_3MgSi_2O_8$)	Ti-6Al-4V	Plasma spraying	Improvement in the corrosion resistance Significant improvement in biological behavior High stability in the body environment Enhancement in the distribution and proliferation of cells cultured on the Ti-6Al-4V alloy The same thermal expansion properties as the Ti-6Al-4V alloy	[236]
	AZ91 Mg alloy	Plasma electrolytic oxidation and electrophoretic deposition	Improvement in biodegradability Slower implant weight loss Reduction in Mg ion released from the coated implants in the blood plasma Lesser release of hydrogen bubbles Improvement in biocompatibility Increase in the amount of bone formation Mild bone inflammation after the surgery Applicable for future clinical applications	[237]
	Ti-6Al-4V	Plasma spraying	Uniform and dense microstructure at the interface of the Ti-6A l-4V surface The thermal expansion coefficient of the coating was adopted to Ti6Al4V alloy	[238]

			Increase in the surface roughness of substrate alloy In vitro and in vivo evaluation of coating is necessary	
Monticellite ($CaMgSiO_4$)	Mg alloy	electrophoretic deposition and plasma electrolytic oxidation	Improvement in the corrosion properties, bioactivity, and cytocompatibility Effective corrosion protection Desired antimicrobial activity Strong adhesion with the PEO coated Mg alloy Homogeneous coating with no obvious cracks or pinholes Reduction in the corrosion rate of the Mg alloy High thickness	[239]
Hardystonite ($Ca_2ZnSi_2O_7$)	Ti-6Al-4V	Plasma spraying	Higher chemical stability and additional antibacterial activity 93% antibacterial ratio against Staphylococcus aureus Significantly improved stability in physiological solution Good bioactivity High bonding strength	[113]
	Ti-6Al-4V	Plasma spraying	Nanostructured surface with grains less than 50 nm in size Higher proliferation rate Hardystonite coatings exhibit a higher proliferation rate than sphene coatings Interfacial bonding of hardystonite coatings is lower than sphene coatings Suitable for orthopaedic application	[240]
	Ti-6Al-4V	Plasma spraying	Improvement in the osseointegration of Ti alloy Improvement in bonding at both coating/implant and coating/bone tissue interfaces Fast in vivo bone formation ability and in vitro functionality Promoting adhesion of canine bone marrow mesenchymal stem cells on the implant surface	[241]
	316LSS	Electrophoretic method	Improvement in the corrosion resistance	[242]

			Less corrosion current density (nine times) Deposition and uniform coatings without cracks	
	Ti-6Al-4V	Plasma spraying	Increase in the antibacterial activity and chemical stability The enhanced antibacterial activity and cell-material interactions are ascribed to slow and constant release of Zn ions Improved chemical stability is contributed to the formation of the stable crystal phase of $Ca_2ZnSi_2O_7$ Improvement in the proliferation and alkaline phosphatase activity	[219]
	Ti-6Al-4V	Plasma spraying	Further efficacy of hardystonite coating in modulating bone formation around the implant Enhancement in osseointegration Enhancement in attachment, proliferation, and differentiation Improvement in chemical stability and biocompatibility Good candidate for orthopedic and dental implant fixation	[243]
	Ti-6Al-4V	Plasma spraying	Higher cell viability and upregulated expression of the osteogenic differentiation genes Having osteoblast-promoting and osteoclast-inhibiting effects to form a dynamic balance between osteoblasts/osteoclasts	[244]
Baghdadite ($Ca_3ZrSi_2O_9$)	Ti-6Al-4V	Plasma spraying	High bonding strength Excellent chemical stability Long-term stability Good apatite-formation ability (good bioactivity)	[245]
	AZ91	Micro-arc oxidation	Dense coating without any cracks Increase in the corrosion resistance Decrease in the corrosion current density of the anodized AZ91 alloy More stable in a physiological environment	[246]
	AZ91	Micro-arc oxidation	Control of the speed of degradability Enhancement in bioactivity and biocompatibility	[247]

			High apatite-formation capability with a controlled release of ions	
Sphene ($CaTiSiO_5$)	Ti-6Al-4V	Plasma spraying	Nanostructured surface with grains less than 50 nm in size Interfacial bonding of sphene coatings is better than hardystonite coatings Sphene coatings exhibit a lower proliferation rate than hardystonite coatings Suitable for orthopaedic application	[240]
	Ti-6Al-4V	Sol-gel process	Significantly improved adhesion strength Significantly improved chemical stability Improved adhesion strength Sphene coatings have the ability to form an apatite layer in SBF	[114]
	Ti-6Al-4V	Sol-gel process	Ability of $Ca_3ZrSi_2O_9$ ceramics to support the adhesion, growth and differentiation of osteoblasts, osteoclasts and endothelial cells without toxic effects	[115]
	Cp-Ti	Spray coating	The reduced amount of defects on the surface of the cryo-machined substrates, contributed to increase the hardness, elastic modulus and adhesion strength of the coating-substrate interfaces compared to standard machined samples Improvement in adhesion Strong interface with no need of secondary operations	[248]
	Cp-Ti	Spray coating	Crack-free coating Uniform morphology of the biocoating Good adhesion strength to the substrate Ideal characteristics for orthopedic and dental implants in terms of adhesion strength and surface roughness	[249]

3.5. Carbon coatings

Both wear and corrosion resistance are essential to increase implant longevity. For example, the creation of wear debris has been associated with the failure of several hip and knee replacement devices. Load-bearing joints, such as hip and knee implants, are expected to endure mechanical loading and high contact pressures in a highly corrosive medium (body fluids) [250]. In order to enhance tribological properties, the development of carbon nanotube (CNT)- or diamond-like carbon (DLC)-reinforced coatings has attracted intensive interest due to their appropriate corrosion protection, excellent wear resistance, self-lubricant nature and proper adhesion strength [250, 251].

The term "diamond-like carbon (DLC)" is attributed to a class of amorphous carbon coatings that exhibits some of the diamond's typical characteristics. Different carbon coatings on metallic biomaterials and their tribological results are compared in **Table 10.** There are various techniques to deposit DLC coatings, such as chemical vapour deposition (CVD) [252], physical vapour deposition (PVD) [253], pulsed laser ablation [254], ion beam deposition [122], and ion beam conversion [123]. Traditionally, CVD takes place at high temperatures (>800 ˚C), but most modern depositions occur at lower temperatures (<400 ˚C). Therefore, a greater range of substrates can be coated at lower temperatures without undergoing unwanted modification/degradation. Each technique can be applied to achieve favorable coating characteristics. For instance, ion beam conversion can be applied to dope DLC coatings with elements such as fluorine, sulfur or nitrogen that serve to decrease friction [124]. DLC coatings need interlayers to strongly bond to the substrate and the DLC surface layer due to high residual stress levels from their structure, which cause poor surface adhesion and early delamination in the coatings [250, 252]. Furthermore, Praveen *et al.* [125] obtained uniform deposition of CNTs on CNTs-Zn composite from a sulfate bath containing dispersed CNTs. The corrosion study revealed a significant increase in corrosion resistance as the CNTs provide a physical barrier to the corrosion environment. CNTs easily fill the micro-pores of the metal surface to enhance corrosion protection as the micro-pores are active sites for metal dissolution.

Table 10. Different carbon coatings on metallic biomaterials and their tribological results.

Carbon coatings	**Coating material**	**Metallic substrate**	**Coating method**	**Tribological results**	**Ref.**
Diamond-like carbon (DLC) coatings	DLC	Steel	Plasma assisted chemical vapor deposition	Reduction in wear rate, coefficient of friction (COF) and fatigue wear	[255]
	DLC	Steel	Pressure sensitive adhesive tape	Better tribological and mechanical properties	[256]
	DLC	AISI 316L austenitic stainless steel	Plasma assisted chemical vapor deposition	Improvement in COF and wear rate	[257]
	DLC	High carbon steel	-	Improvement in hardness and formation of iron carbide	[258]
	DLC	Ti6Al7Nb	Arc ion plating/ magnetron sputtering	Better corrosion resistance	[259]
	DLC	Ti6Al4V	Cathodic arc vapour deposition	Low COF and wear rate	[260]
	DLC	Ti6Al4V	Cathodic arc coating	Improvement in friction and wear rate	[261]
	DLC	Ti6Al4V	Plasma immersion ion deposition/ plasma magnetron sputtering	Reduction in wear rate and COF	[262]
	DLC	Mg alloy	Radio frequency sputtering	Uniform distribution and improvement in corrosion and wear resistance	[263]
Carbon nanotubes (CNT) coatings	CNTs	Polyethylene oxide	Spin coating	Improvement in COF and wear rate	[264]
	CNTs	CNTs-Zn	Electrophoretic deposition	Uniform deposition and good corrosion resistance	[125]
	MWCNTs	Ni	Electrophoretic deposition	Uniform distribution and improvement in tribological properties	[265]
	MWCNTs	Ti plate	-	Low and stable friction coefficient	[266]
	CNTs-Ag	Silicon wafer	Spin/ electroless coating	Improvement in COF and wear rate	[267]
	Ti/MWCNTs	Ti alloy	Laser deposition	Improvement in TiC dendrite	[268]

	Co-Ni/MWCNTs	Cu plate	Electrophoretic deposition	Excellent wear resistance	[269]

4. Conclusions and future directions

There is a clear consensus that the coating of the metallic implants with bioceramics improves bioactivity, corrosion resistance, bone-bonding ability, and many other essential attributes in implantology. However, the limits of present orthopedic/dental implants and prosthetic components need to be still overcome by developing better coatings for the biofunctionalization of metallic surfaces, which at the same time requires leaving intact excellent mechanical properties of metallic biomaterials. These requirements could be satisfied if biocompatible bioceramics are applied on the metallic surface. As witnessed by the large number and variety of studies published in the literature and reviewed in this article, the number of bioceramic coating applications on metallic implants has expanded dramatically in the last few years. A large number of methods have been reported to design and develop implant coatings. The choice and application of a specific processing method should be guided by the workability of the coating material and its physico-chemical/biological properties, taking into account that the procedures involved in coating fabrication/manipulation should be helpful in the tissue regeneration process.

Another issue deserving careful attention is that the assessment and comparison of the performance of bioceramic coatings applied onto “real” substrates with complex shape and curved profiles is not easy since often there is a lack in the definition of standard methods or protocols to evaluate and characterize the properties of coatings deposited on non-flat geometries.

In testing bioceramic coatings, further consideration of the dynamic environment in the human body should be explored because different types of ceramics are exposed to different environments. Additionally, further pre-clinical studies using models based on different defect locations should be standardized.

Looking at the future, several approaches can be suggested to optimize the design and development of bioceramic coatings for medical applications. In this regard, multi-layered, nature-inspired coatings could open a new horizon into the future of multifunctional biomedical implants. Each layer or complex biomimetic structure can trigger a unique functionality.

We also observed that available *in vivo* or clinical trials on metallic implants coated with bioceramics are limited. Therefore, it is still inevitable to expand the knowledge on the effects of chemical composition, surface features and mechanical properties of the coatings *in vivo* and clinical studies.

Future studies should aim to create therapeutic coatings with multi-beneficial effects such as osteoconductive/osteoinductive properties combined with the ability to deliver therapeutic ions, proteins, growth factors, and drugs. These extra-functionalities will enhance coating ability to stimulate bone growth, hinder infection, and, eventually, increase implant lifetime.

Another worth-study approach is deeply investigating the molecular mechanisms involved in the cell-coating interactions, such as the interaction between organic (proteins) and inorganic (structure of ceramics) interfaces.

Finally, novel composite or organic-inorganic hybrid coatings could still be developed by combining bioceramics and biopolymers in order to optimize the biological interactions with bone and tissues as well as to finely modulate coating resorption rate and, hence, the therapeutic action.

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