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**Chapter**

# Surface Science Engineering through Sol-Gel Process

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## Abstract

Sol-gel synthesis is used to obtain coatings that can modify the surfaces of metals to avoid corrosion or to enhance the biocompatibility and bioactivity of metals and their alloys that are of biomedical interest. Anticorrosion coatings composed of smart coatings and self-healing coatings will be described. $TiO_2$, hydroxyapatite, bioglass, and hybrid coatings synthetized by sol-gel technology will be briefly introduced with regard to their role in surface-modifying metals for biomedical purposes. Finally, although there are other approaches to surface-modifying metals for either anticorrosion or biomedical purposes, sol-gel methods have several advantages in controlling surface chemistry composition and functionality.

**Keywords:** surface modification, coatings, sol-gel, corrosion, biomaterials

## 1. Introduction

The need to control interactions between materials and their surrounding environment is mainly concerned with the surface properties of these materials. In this sense, the sol-gel process is being increasingly used to surface modify a wide range of materials such as metals, organic polymers, inorganic particles, and glasses, where wettability, biocompatibility, porosity, corrosion, catalytic activity, and selective adsorption of analytes can be controlled at the required substrate surfaces. For this reason, sol-gels have gained attention in different scientific and technological fields, including metallurgy, biomaterials, analytical chemistry, and photocatalysts. In this chapter, an overview of sol-gel chemistry and its applicability to modifying the surfaces of metals and their alloys for anticorrosion and biomedical purposes will be presented.

## 2. Sol-gel chemistry

The sol-gel technology is a technique that has been widely employed in the synthesis of inorganic polymers or advanced organic-inorganic hybrids due to versatile and simplicity. Two chemical reactions are involved, hydrolysis and condensation,

and these produce a variety of organic-inorganic networks from precursor monomers such as silicon alkoxide or metals alkoxides [1, 2]. This technique permit to obtain materials in any form and to it is possible to produce homogeneous materials with the desirable properties of toughness, high purity, optical transparency, chemical stability, controlled porosity, and thermal resistance at room temperature and low cost [3].

The sol-gel process, as the name implies, is the transition of a liquid colloidal solution (sol) to a solid three-dimensional matrix (gel). The precursors for the synthesis of these colloids consist of a metal or metalloid element surrounded by several reactive ligands. Metal alkoxides are the most popular, since they react easily with water. The most extensively used are the metal alkoxides and the alkoxysilanes, such as tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS). Nevertheless, other alkoxides such as aluminates, titanates, and borates are also commonly used in the sol-gel process, where they are often mixed with TEOS [1].

The most widely used method is the organic approach, which generally starts with a solution of monomeric metal or metalloid alkoxide precursors, $M(OR)_n$, in an alcohol or another low-molecular-weight organic solvent. Here, M represents a network-forming element such as Si, Ti, Zr, Al, Fe, and B, while R is typically an alkyl group ($C_xH_{2x+1}$) [4].

The sol-gel process involves a transition from a liquid colloidal solution (sol) to a solid three-dimensional matrix (gel). The precursors for the synthesis of these colloids consist of a metal or metalloid element surrounded by several reactive ligands. Metal alkoxides are the most popular due to their affinity with water. Among the most used alkoxylated agents are tetramethoxysilane (TMOS), tetraethoxysilane (TEOS), and alkoxides such as aluminates, titanates, and borates mixed with TEOS [1].

In the hydrolysis reactions (**Figure 1(1)**), alkoxide groups (—OR) are replaced with hydroxyl groups (—OH) through the addition of water. Subsequent condensation reactions (**Figure 1(2a)** and **(2b)**) involve the silanol groups (Si—OH), which create siloxane linkages (Si—O—Si) and subproducts such as water and alcohol. The condensation reaction starts before the hydrolysis has been completed. However, conditions such as the pH, $H_2O$/Si R and catalyst can force the hydrolysis to end before the condensation starts [3].

The use of an alcohol favors hydrolysis, causing the miscibility of the alkoxide and the water [3]. As the number of siloxane linkages increases, the individual molecules are joined to one another and aggregated into the sol. When the sol's particles are interlocked into a network, a gel is formed. A drying stage in which volatile components such as water and alcohol are extracted from the network is necessary, causing the gel to shrink while condensation occurs. It should be noted, however, that the addition of solvents and certain reaction conditions can promote esterification and depolymerization reactions, in accordance with the reverse reactions
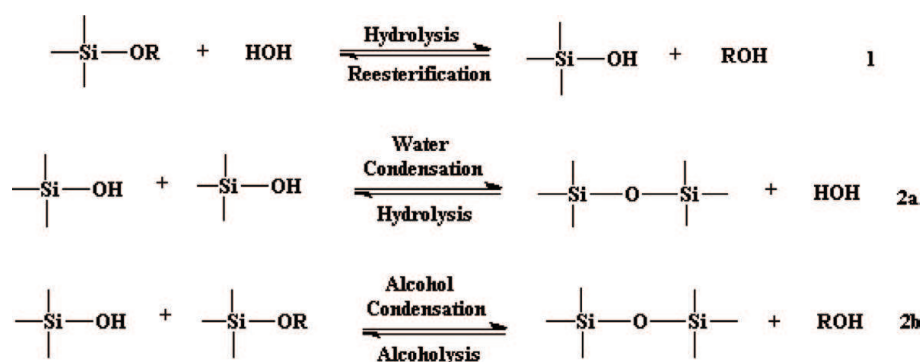


**Figure 1.**
*General schematic of the hydrolysis and condensations of alkoxides.*

(**Figure 1(2a)** and (**2b**)) [1, 3]. More specifically, factors such as the pH, nature and concentration of the catalyst, and $H_2O/Si$ R play the most important parts in the final structure and properties of the obtained hybrid polymeric network [1]. In this section, the effect of pH will be described, as controlling the pH of sol-gel media is generally used to obtain either coatings or powders; however, readers can find a detailed mechanism in specialized reviews or books on sol-gel chemistry.

Drying involves the loss of water, alcohol, and other volatile components. During drying, the gel initially shrinks due to the loss of pore fluid that maintains the liquid-vapor interface on the outer surface of the gel, this occurs always under atmospheric conditions. The liquid-vapor meniscus recedes toward the interior of the gel, in the final stage of drying [5]. When the drying is under supercritical conditions, the surface tension disappears with a gradient of capillary pressure accumulated in the walls of the pores, which avoids the possible collapse of the volume of the pores due to the capillary forces. Under these conditions, the materials are left with a wet porous texture that prevents the collapse of the pores of the gel, and the resulting materials are generally hydrophobic, because their surfaces are covered with alkoxy groups [6].

## 2.1 Sol-gel coatings

For anticorrosion and biomedical applications, several techniques are used to surface modify metals to improve their mechanical properties, enhance their corrosion resistance or, in some cases, give biological, osteoconductive, or antibacterial activity. Among these techniques are physical vapor deposition (PVD), chemical vapor deposition (CVD), and electrophoresis, and sol-gels can be used to surface modify metal [7]. However, the versatile methodology of sol-gel synthesis generates diverse types of materials that have found applications in several scientific and technical fields [8]. It is precisely this versatility that has generated great interest in using sol-gel techniques to develop coatings that are applied in areas such as analytical chemistry to develop more efficient, specific sorbents that allow the concentration of desired analytes [9–11]. In biomedical fields, sol-gel coatings have gained attention in controlling the surface interactions between medical implants/devices and biological environments [12, 13]. In the field of photocatalysis, sol-gel coatings have been developed for applications such as for organic compound degradation [14]. Anticorrosion sol-gel coatings have been applied to avoid degradation of materials and metallic structures to prevent or preserve the surface and bulk integrity of metallic materials [15].

The sol-gel coating technique consists of the immersion of a substrate that is to be coated in the "sol" solution and the vertical extraction of this substrate at a controlled speed [13]. A very fine coating of gel is thus formed, since there is rapid evaporation of the solvent during the extraction of the substrate. The thickness depends on the viscosity of the liquid, the surface tension, and especially the speed of removal; the higher the speed of removal is, the greater the thickness of the coating [16]. Once the first coating layer is obtained, the process can be repeated to form a multilayer structure. The drying step also influences the final structure of the film, and there are thickness limits that must be obeyed to avoid the cracking of films or their detachment from the substrate [17].

## 3. Sol-gel coatings for anticorrosion purposes

According to the standard ISO8044:2015, corrosion is defined as a spontaneous degradation of metals due to their physicochemical interaction with the surrounding environment, which changes the properties of the metal and can lead

to its functional destruction. The main cause of the corrosion of metals is their thermodynamic instability in outdoor conditions. As a result, metals are converted into compounds (oxides, hydroxides, carbonates, sulfides, etc.) that, as corrosion products, are the most stable forms of the metal. In this way, corrosion leads to a decrease in Gibbs free energy and therefore occurs spontaneously. Generally, coatings are designed to stop corrosion of metals by one of the following mechanisms: cathodic protection, anodic passivation, electrolytic inhibition, environmental modification, plating, painting, and active corrosion inhibition [18, 19].

Using coatings to protect metallic substrates from corrosion is an active and important research area in materials science and industry. Through the application of coatings, corrosion can be minimized and controlled; the coating acts as a barrier preventing contact between the corrosive medium and the metallic substrate and preventing ion migration among the coatings; in addition, in cathodic protection, the coating material acts as a sacrificial anode. The use of species for inhibition/passivation, including cases of anodic and/or cathodic protection, inhibits the action of external corrosive agents. The sol-gel process stands out among the many other coating methods, e.g., CVD [20], PVD [21], electrochemical deposition [22], plasma spraying, and others [23]. The sol-gel coating process generally involves temperatures close to room temperature; thus, thermal volatilization and degradation of entrapped species, such as organic inhibitors, is minimized. Since liquid precursors are used, it is possible to cast coatings in complex shapes and to produce thin films without the need for machining or melting. The sol-gel films are formed by "green" coating technologies, which use compounds that do not introduce impurities into the product; this method is waste free and lacks a washing stage. The interest in this type of material has increased exponentially in recent decades.

## 3.1 Organic-inorganic hybrid coatings

Organic-inorganic hybrid (OIH) coatings created by the sol-gel process are very suitable for resisting corrosion. Inorganic sols in hybrid coatings not only increase adhesion by forming chemical bonds between metals and hybrid coatings but also improve the comprehensive performance of polymers in the coatings. Different organic polymers or organic functionalities are introduced into the gel network to produce tailored properties such as hydrophobicity and increased crosslink density. For corrosion protection of metals, organic components of hybrid coatings are selected to repel water, form dense thick films, and reduce coating porosity. Factors such as the ratio between inorganic and organic components in hybrid coatings, cure temperature, and pigment-related parameters need to be optimized as a function of the specific metal for the production of hybrid films with maximum corrosion resistance [24].

Sol-gel OIH coatings are macromolecular matrices where the intermolecular interactions (such as porosity, rigidity and adhesion to the substrate, among others) between its structure and the metal surface are very relevant for the final properties of the material. The better it is combination between OIH coatings and the substrate results in materials with improved protection against corrosion, oxidation and erosion, and good electrical and thermal insulation properties. Sol-gel OIH coatings are commonly produced by gels obtained from the gelation of colloidal solutions, hydrolysis and polycondensation of precursors, and their subsequent aging and drying [25].

Sol-gel OIHs based on siloxanes (Si—O-metal oxide), alkoxysilanes and alkoxides of zirconium, titanium, cerium, tin, and aluminum are potential candidates for the treatment of steel surfaces, allowing covalent bonding between the inorganic parts of the OIHs and the metallic substrate.

For iron-based alloys, steel is the most common and versatile metal, and the corrosion resistance behavior of sol-gel coatings deposited on these substrates has been extensively studied. Publications have mostly focused on the use of TEOS, 3-glycidoxypropyl-trimethoxysilane (GPTMS), methacryloxypropyl trimethoxysilane (MAPTS), and methyltriethoxysilane (MTES) and have sometimes included the performance of coating materials with embedded corrosion inhibitor species. For example, Santana et al. used clay nanoparticles to improve mechanical and barrier properties and Ce as an inhibitor for OIH sol-gel coatings [26]. Generally, the reported studies show that those OIH coatings exhibit a promising performance against corrosion in iron-based alloys [27]. The use of different organosilica sol-gel coatings on steel substrates has been reported. The results indicate that it is possible to tailor the sol-gel composition to modify coating properties such as hydrophobicity, wettability, adhesion, and corrosion prevention. Precise selection of organically modified sol-gel compositions has yielded coatings that are adhesive, water-repellent, and effective at preventing corrosion of coated steel panels.

OIH sol-gel coatings are an excellent choice for aluminum-based alloys because in addition to the OIH properties; these materials can provide a stable Si—O—Al bond between the inorganic functionality of these materials and the formed passivation layer. Previous work in the literature focuses on the use of TEOS and GPTMS, the performance of coating materials with encrusted corrosion inhibitor species, and the deposition of multilayers by several cycles of deposition curing [25, 28]. Cambon et al. investigated modifications of OIH sol-gel coatings using different amounts of cerium, studied how these coatings protected different aluminum-based alloys from corrosion with electrochemical methods, and reported improvements in the anticorrosion process by increasing the concentration of cerium in OIH sol-gel coatings [29].

For copper and copper-based alloys, the use of OIH coatings did not give very good results with respect to corrosion, but the use of TEOS and GPTMS with 1,2,3-benzotriazole resulted in a corrosion inhibitor effective in different environmental media. For zinc-based alloys, few studies have used OIH sol-gel coatings, and GPTMS, TEOS and MTES have been used as precursors to focus on new green conversion coatings based on molybdate, permanganate, silicate, titanate, rare earth salt, tungsten, and vanadate compounds. Finally, for magnesium-based alloys with OIH coatings, the reported literature mainly focuses on the use of GPTMS in combination with other reagents, especially (3-aminopropyl) triethoxysilane (APTES). For this material, the inorganic component is selected to form the network for the film, while the organic component is selected to repel water and fill the porosity shortly. These hybrid coatings have excellent mechanical strength and adhesion to metal substrates. Hybrid coatings doped with slow release corrosion inhibitors provide long-term metal anticorrosion. Superhydrophobic coatings are an excellent option to resist corrosion, and their properties are derived from the low surface tension and roughness of the surface of hybrid coatings, although it is necessary to prolong their durability. It is obvious that the combination of these techniques can provide superior anticorrosive properties [24].

Despite the advantages of combining different properties in these materials, synthesis constraints remain. The major limitations of sol-gel processing for coating metals are delamination, crackability, adhesion, and thickness limits. Assuring a uniform distribution on the substrate and optimizing thermal treatments (curing/drying) are crucial factors to ensure the quality of anticorrosive coatings.

**3.2 Smart coatings**

Active corrosion inhibition addresses the unavoidable failure of coatings and includes the introduction of components that release selectively during damage to

the coating to reconstruct a protective barrier at the metal-environment interface. Such active corrosion inhibition is different from the broader concept of "self-healing," which also includes the introduction of materials that are released within the coating that allow for reformation of polymeric organic coatings even without direct protection from corrosion [18].

Functional coatings (organic, inorganic, or hybrid) are a new class of materials that can be adapted for many applications in which they should be able to perform well-defined arrays of functions. The concept of a smart coating is more recent and has been applied to functional coatings that can respond to certain stimuli generated by surroundings [30]. Functional and smart coatings have been regularly reviewed for various applications, including active corrosion protection and inhibition. However, summarizing the progress in this area requires a concise review of the latest trends. The application of functional and smart coatings is one of the most promising routes to developing active corrosion protection and inhibition systems. Two main strategies have been pursued to introduce the required functionalities into coatings: encapsulation/loading of functional active species in host carriers and manipulation of the coating matrix composition for inclusion of bulk and/or surface functional groups. In this case, intelligent self-healing coatings are coatings whose suitable repair agents are safely stored but can be released on demand, i.e., when corrosion occurs and only then [31].

### 3.3 Self-healing coatings by sol-gel methods

Self-healing materials are well known as materials that are capable of autonomously restoring their properties in such a manner that they can function longer than similar materials without self-healing abilities. Self-healing coatings are required for the total or partial repair of coated areas damaged by aging or unexpected aggressive events. Two main strategies have been pursued regarding self-healing coatings for corrosion protection: (i) mending defects formed in the polymeric coating matrix via addition of polymerizable agents and (ii) inhibition of corroding areas due to the presence of corrosion inhibitors [32, 33]. Usually, the self-healing agent is released because of mechanical damage. However, not all mechanical damage leads to corrosion, and corrosion is not necessarily initiated at mechanical cracks. Ideally, the release of self-healing agents should take place only when corrosion is initiated. Triggers for sensing the corrosion of a metal system that have been investigated in depth are pH and ionic strength changes. However, the most reliable and case-selective trigger is a change in the electrochemical potential, as it always decreases when corrosion occurs [31].

Currently, the literature exhibits many reports of the encapsulation of agents for protection against corrosion that have self-healing capacity activated by different extrinsic or intrinsic stimuli, which can be local pH gradients, capsule rupture induced by mechanical stress, ion exchange processes, water trapping, electrochemical potential changes, light irradiation, thermal variations, and others; in some cases, neither the kinetics of healing nor the mechanisms are completely understood [30]. Below, some self-healing coatings for corrosion protection that were obtained by the sol-gel technique and have been applied on aluminum substrates are presented.

Snihirova and coworkers investigated inhibitor-doped hydroxyapatite (HAp) microparticles that were used as reservoirs, storing corrosion inhibitors to be released on demand. Release of the entrapped inhibitor was triggered by redox reactions associated with the corrosion process. HAp was used as reservoirs for several inhibiting species, Ce(III), La(III), salicylaldoxime, and 8-hydroxyquinoline, which are effective corrosion inhibitors for 2024 aluminum alloy (AA2024).

Dissolution of the microparticles and release of the inhibitor were triggered by local acidification resulting from an anodic half-reaction during corrosion of AA2024. Calculated and experimentally measured local acidification at the aluminum anode (down to pH = 3.65) were presented. The anticorrosion properties of inhibitor-doped HAp were assessed using electrochemical impedance spectroscopy. Microparticles impregnated with corrosion inhibitors were introduced into a hybrid silica-zirconia sol-gel film, which acted as a thin protective coating for AA2024, an alloy used for aeronautical applications. The protective properties of the sol-gel films were improved by the addition of Hap microparticles, proving their applicability as submicrometer-sized reservoirs of corrosion inhibitors for active anticorrosion coatings. The synthesis of HAp from solutions of calcium nitrate and ammonium hydrophosphate was carried out with the addition of citric acid to modulate its morphology. The obtained solution was placed in a water bath at 37°C for 24 h, allowing the precipitation of HAp. Once the HAp particles were obtained, they were immersed in solutions containing Ce(III), La(III), salicylaldoxime, and 8-hydroxyquinoline. Hybrid silica-zirconia sol-gel films were obtained by combining an organosiloxane alkosol with another alkosol containing a zirconia. The silane-based alkosol was prepared through hydrolysis of GPTMS in 2-propanol by adding a diluted aqueous solution of $HNO_3$ at room temperature for 1 h. The second alkosol, containing zirconia nanoparticles, was prepared through controlled stoichiometric acidic hydrolysis of a 70 wt% 2-propanol solution of Zr(IV) tetrapropoxide in ethyl acetoacetate under ultrasonic agitation. Finally, the two alkosols were mixed in a 2:1 volume ratio, ultrasonically agitated for 1 h and then aged for another 1 h at room temperature [34]. According to their results, HAp presents a good chemical stability and compatibility with the sol-gel matrix, sufficient loading capacity, an ability to sense corrosion onset (local acidification), and an ability to release the inhibitor on demand [34].

Li and coworkers have reported the incorporation of environment-responsive properties into tube-like nanomaterials in self-healing coatings for corrosion protection. Stimulus-responsive silica/polymer double-walled hybrid nanotubes with a controlled aspect ratio (length/diameter) were synthesized by surface-graft precipitation polymerization. The surface grafts on the hybrid nanotubes consisted of pH-, temperature-, or redox-responsive polymers that can confer a smart stimulus-responsive property upon the hybrid nanotubes. In addition to their well-defined morphology, uniform size, and wall thickness, the as-prepared silica/polymer hybrid nanotubes exhibited release in response to these different environmental stimuli. The silica/polymer double-walled hybrid nanotubes serve as intelligent nanocontainers of the anticorrosion agent benzotriazole.

The silica/polymer double-walled hybrid nanotubes served as smart nanocontainers, which is very important for applications in self-healing coatings [35]. Self-healing coatings were prepared by dispersing the as-obtained nanotube containers into SiOx/ZrOy hybrid films at room temperature. The SiOx/ZrOy hybrid films doped with benzotriazole-loaded $SiO_2$/PMAA nanocontainers were prepared by a sol-gel process. In this case, a zirconium oxide sol was prepared from a tetra-n-propoxy zirconium (TPOZ) solution (70 wt% 2-propanol) in ethylacetoacetate at room temperature. The second organosiloxane sol was prepared by hydrolyzing 3-chloropropyltrimethoxysilane (CPTMS) in 2-propanol by the addition of acidified water ($HNO_3$, pH 0.5). Then, the zirconia sol and organosiloxane sol were mixed, stirred and aged at room temperature. BTA-loaded nanotube containers were mixed with the SiOx/ZrOy films at a concentration of 10 mg/mL by sonication. Self-healing films were fabricated on carbon steel by a dip-coating procedure. The carbon steel was immersed into the sol-gel mixtures and then withdrawn, and the samples were cured at 130°C [35].

As you will see in detail later, corrosion is an important factor in the design and selection of alloys for application in vivo. Because toxic species might be released to the body during corrosion and various corrosion mechanisms can lead to implant loosening and failure, biomaterials are often required to be tested for corrosion and solubility before they are approved by regulatory organizations.

## 4. Sol-gel coatings applied to biomaterials

A biomaterial is any substance that has been engineered to interact with biological systems for a medical purpose, such as a therapeutic (which treats, augments, repairs, or replaces a tissue function of the body) [36–38]. Metals [23], polymers [39], ceramics [40], and their combinations [41] can be used as biomaterials. Among the different kinds of biomaterials, metal implants have been used with success in orthopedic applications, as well as temporary appliances such as pins, screws, and bone plates and permanent implants such as total joint substitutions.

An implanted material could have a desired or undesired biological response depending on its surface characteristics such as wettability, charge, topography, and surface chemistry [42]. These surface properties are the major factors that ultimately determine the rejection or acceptance of a biomaterial in the body because the surface is the interface where the biomaterials meet and interact with the biological environment (i.e., bone, soft tissue, and blood). For this reason, surfaces of these metals must be modified; otherwise, the body will recognize those implants as foreign and isolate them in a fibrotic capsule, compromising their overall performance [43]. Surface modification of these metallic surfaces is engineered and designed to improve tissue tolerance, osseointegration, and corrosion [44]. Among the different surface modification technologies, such as grist blast [45], chemical etching [46], and plasma surface modification [47], the application of sol-gels has also been shown to improve the biocompatibility of metal implants [48].

Osseointegration is defined as "the direct structural and functional connection between the ordered, living bone and the surface of a load-carrying implant" [49]. The sol-gel process allows the chemical composition of its products to be controlled, resulting in greater bioactivity than those materials with the same composition but prepared with different methods [13]. The intrinsic bioactivity of sol-gel materials together with their possibility of being coupled with a range of coating techniques, e.g., dip, spin, and spray coating, makes sol-gels an ideal technology in the making of bioactive and biocompatible coatings [13].

In this section, $TiO_2$, HAp, bioactive glasses, and hybrid composite coatings synthetized by the sol-gel technique to surface-modify metals of biomedical interest for implants will be described.

### 4.1 Hydroxyapatite (HAp) as a sol-gel coating

HAp ($Ca_{10}(PO_4)_6(OH)_2$) is a biocompatible and bioactive material that can be used to restore bony defects [50–52]. Because of its chemical and structural similarities to the inorganic phase of human bone, HAp shows excellent biocompatibility. Most of the relevant applications of this material take advantage of its biological influence on tissues and especially its biodegradation behavior. Conventionally, HAp powders are synthesized via precipitation from an aqueous solution, solid-state reactions, and hydrothermal methods. However, these powders are sometimes unsuitable for the preparation of HAp ceramics with controlled biocompatibility and bioactivity because of their chemical and phase heterogeneity [53–58].

One of the most important issues when considering HAp for biological coatings is its dissolution rate in human body fluids. Plasma-sprayed HAp coatings dissolve and degrade quickly, resulting in the weakening of the coating-substrate bonding or implant fixation to host tissues [59, 60].

Sol-gel synthesis of HAp ceramics has recently attracted much attention because of its advantages: it provides a molecular-level mixing of the calcium and phosphorus precursors and is capable of improving the chemical homogeneity of the resulting mineral composite in comparison with the products from conventional solid-state reactions, wet precipitation, and hydrothermal synthesis [55–57, 61, 62].

The sol-gel process provides an alternative to conventional synthesis methods. The metal alkoxides, $M(OR)_n$, convert to amorphous gels of metal oxides through hydrolysis and condensation reactions. The sol-gel materials are transformed into ceramics by heating at relatively low temperatures and have better chemical and structural homogeneity than ceramics obtained by conventional methods.

Pathway alkoxide-based considers an anhydrous medium, where precipitation of unwanted calcium phosphate phases can be slowed down, and the molar concentration of the reactive species can be heightened relative to a point that benefit the mineral development before the start of the reaction. Likewise, chelation-based sol-gel methods preserve a good degree of control, preventing the precipitation.

The synthesis of pure HAp requires the same molar ratio between calcium and phosphate as in the final product. The temperature required to form the apatite structure depends on the chemical nature of the substrate. Low-temperature synthesis particularly benefits the metal substrates (temperatures below 500°C).

The conditions to obtain the best coatings have been related to the pH decrease that occurs in aqueous sols during aging, which is based on the polymerization reaction between calcium and phosphorous. To obtain homogeneous, crack-free coatings, the annealing temperature and thickness of the coatings should also be controlled. Film roughness is related to the viscosity of the sol-precursor used for deposition and the number of coating layers. Thus, depending on the exact application, various parameters of the applied coating can be adequately controlled.

Prepared HAp sols and Ag-doped HAp sols have been coated on passivated Ti surfaces by spin coating at 5000 rpm for 50 s. The coated Ti surfaces were immediately dried at 70°C for 12 h and then heat-treated at 650°C for 3 h. HAp without Ag doping was used as controls in this study. All samples were autoclaved prior to material characterization and all culture experiments [63].

Overall, it was concluded that the material AgHA1.0 has similar biological activity as HAp with respect to bone cell proliferation and differentiation. In addition, AgHAp 1.0 also minimizes the initial bacteria adhesion [63].

Caution should also be taken in applying HAp-coated materials to patients, since an HAp coating was found to have negative effects on bone formation. Reports in the literature [64, 65] have suggested that HAp coatings are unstable, susceptible to bacterial infection, possibly predisposed to rapid osseous breakdown, and absent of significant advantages over titanium implants [66].

To obtain bioactive materials with high mechanical strength, metal implants (titanium and stainless steel (SS) alloys) are usually coated with a thin layer of HAp using plasma spray techniques [67–69]. The main problem associated with this technique is a lack of exact stoichiometry control and the occurrence of glassy phases in the ceramic layer. Some of these additional phases do not show bioactive behavior or do not dissolve in biological environments [69].

For the above, various techniques have been described as effective means of surface treatment and corrosion resistance enhancement of NiTi implants, including chemical passivation, electropolishing, anodization, thermal oxidation, laser surface melting, nitriding, plasma ion implantation, and coating with sol-gels [70–75].

Out of these, the sol-gel route for surface modification of Ti implants is of particular interest because of simple and inexpensive methodology, low temperature processing, and suitability for coating substrates of irregular shapes, such as implants [76–78].

## 4.2 Titanium dioxide (TiO$_2$) as a sol-gel coating

TiO$_2$ is a very interesting material due to its technological applications in biomaterials. An example of this is sol-gel-derived titania and its coatings, which are bioactive materials, and are used in applications as diverse as biomaterials [79, 80]. Advantages of sol-gel processes over other methods are their controlled transformation of the microstructure of the deposited film. Today microstructure control is needed for many applications and the use of sol-gel routes opens up new possibilities.

In common sol-gel methods for preparing TiO$_2$ materials, highly reactive alkoxide titanium precursors are violently hydrolyzed and further condense to form a Ti—O—Ti network. Unfortunately, this route can lead to precipitation of amorphous particles with uncontrolled structures. To overcome many of the specific problems of sol-gel methods employing water as the hydrolysis agent and to control hydrolysis and polycondensation reactions, the application of nonhydrolytic methods, ionic liquids, organic additives, and coordination chemistry have been attempted [81–83].

On the other hand, it has been reported that TiO$_2$ films can effectively improve corrosion resistance and biocompatibility [84–86]. An example of this is given in titania films on biomedical steel exhibit anticorrosion properties in physiological solutions [87, 88]. At present, resistant sol-gel TiO$_2$ coatings synthesized by heat treatment under low temperature have received good results for the preparation of anticorrosive and bioactive coatings to protect metal implants.

The desired properties can be obtained by careful control of reaction conditions or by the use of suitable additives [89]. Moreover, sol-gel processing offers a unique opportunity to prepare layers at low temperatures so that an essential part of the sol-gel preparation process is the thermal treatment that is necessary to form pure TiO$_2$ films.

Conventional metal implants can be surface modified with sol-gel coatings, but organic synthetic polymers such as polyether-ether-ketone (PEEK) can also be surface modified with TiO$_2$ sol-gel-derived coatings to overcome low bioactivity due to their chemical inertness, which is characteristic of most synthetic organic polymers. These sol-gel-derived TiO$_2$ coatings showed greater bone bonding ability than PEEK [90].

However, to avoid corrosion, a TiO$_2$ dip-coating method and its variants are commonly used for the deposition of TiO$_2$ sol-gel-derived coatings onto metal implants [91]. For example, an NiTi surgical alloy was surface modified with thin films of TiO$_2$ to improve corrosion resistance, but these films also showed blood compatibility in vitro [92]. Avoiding corrosion and improving biocompatibility with surrounding tissues are not the only ultimate goals of sol-gel-coating metals of biomedical interest, avoiding the release of toxic ions, possibly through degradation, that some alloys may contain is another such goal [92].

With respect to annealing time and temperature in sol-gel coatings, both parameters exhibit a dependence with the degradation rate, as studied in the TiO$_2$ sol-gel deposited onto a magnesium alloy (AZ31), where the treatment with low annealing temperatures decreased the corrosion rate. Long-time treatment of annealing helped to enhance corrosion resistance [93].

TiO$_2$ sol-gel coatings doped with a high calcium ion concentration showed better corrosion resistance for M30NW biomedical alloy substrates in a simulated body fluid (SBF) test than similar coatings with low calcium ions concentrations [94].

## 4.3 Sol-gel-derived bioactive glass coatings

Bioglasses are a family of materials that have shown bioactivity for bone repair and can bond with living bone [95]. In 1971, the first bioglass named 45S5 was discovered by Hench, and since then, many other glass compositions have been developed. Bioglass 45S5 is composed of 45 wt% SiO$_2$, 24.5 wt% CaO, 24.5 wt% Na$_2$O, and 6.0 wt% P$_2$O$_5$, but other similar composition has been used and in some cases enhancing components can be added [96]. Bioglass 45S5 compositions have been shown to be optimal for biomedical applications because it is similar to that of HAp, the mineral component of bone. Ca/P ratios in SiO$_2$·CaO·P$_2$O$_5$ glasses coatings can be controlled with stoichiometric control of TEOS, calcium nitrate tetrahydrate (Ca(NO$_3$)$_2$·4H$_2$O), and triethyl phosphate (TEP) as sol-gel precursors [97]. Coatings with higher Ca/P ratios showed that greater cell proliferation, however, growth inhibition was observed in response to a low Ca/P-ratio in coating compositions [98].

The surface of a bioglass implant, when subjected to an aqueous solution or body fluids, converts to a silica-CaO/P$_2$O$_5$-rich gel layer that subsequently mineralizes into hydroxycarbonate in hours [99–101]. Bone tissue growth improved with increasing dissolution [102]. This gel layer resembles the HAp matrix so much that osteoblasts were differentiated and new bone was deposited [103].

Bioglasses are the most promising materials for bone grafting in several clinical applications such as orthopedic, dental, maxillofacial, and otolaryngological applications [104].

From a synthetic point of view, bioglasses can be prepared either by melting or sol-gel methods, which affect their physical and biological properties [105], but it is also important to define the methods of coating preparation or deposition affecting the ultimate performance of the coatings. Bioglass coatings are usually deposited onto metals or alloys using sol-gel [106], electrophoretic deposition [107], laser cladding [108], and thermal spraying (plasma spraying and high-velocity oxy-fuel) techniques [109]. The technique most employed to spray bioglass since 1980 is thermal spraying and specifically atmospheric plasma spraying, due to its low cost and industrial feasibility [110, 111].

Sol-gel-derived bioglasses are excellent materials for use in tissue engineering applications, such as covering prosthetic metallic implants. Recently, porous bioactive glasses have been derived through sol-gel processing in an attempt to increase the specific surface area and thus the surface reactivity and degradability of the material. This approach allows the material to be replaced ultimately by natural tissue while stimulating bone regeneration [97].

The sol-gel technique can be used to coat 316 L SS [112], titanium [4], and magnesium biomedical alloys [106] with bioactive glass or derived glass-ceramic.

For example, the formation of an apatite layer assures the bioactivity of the bioglass coating, which also improves the corrosion resistance of 316 L SS substrates. Bioactive glass-coated 316 L SS showed greater pitting corrosion resistance than pristine samples. It was concluded that by using the bioactive glass-coated 316 L SS as a human body implant, improvement of corrosion resistance, as an indication of biocompatibility, and bone bonding could be obtained simultaneously [112]. Uncoated 316 L SS possesses high corrosion current density (Icorr = 265 nA/cm$^2$) and thus low corrosion resistance in normal saline solution [112].

Relatively dense sol-gel coatings can be obtained with postheat treatment, causing a substantial volume contraction. In parallel, residual stress gradually

accumulates at the interface between the coating and the substrate [113], remarkably affecting bond strength and the corrosion resistance of samples [114]. Therefore, heat treatments must be carefully controlled and optimized to obtain favorable bonding properties as well as corrosion resistance for sol-gel-derived coatings on magnesium alloy implants [106].

The sol-gel process is carried out at much lower temperatures than traditional melting methods. Because of the low fabrication temperatures used in this method, the composition and homogeneity of the product are greatly controlled. Higher mesoporosity and surface areas are obtained in sol-gel-derived bioglasses than in melt-derived bioglasses, which exhibit high glass transition temperatures [105].

## 4.4 Organic-inorganic composite hybrid coatings

Inorganic sol-gel coatings are brittle, which can compromise their performance. To overcome this drawback, an organic polymer can be entrapped in an inorganic sol-gel glassy matrix to form an OIH sol-gel nanocomposite coating that can be deposited onto different metals and their alloys of biomedical interest. Poly-ε-caprolactone (PCL) [13], poly(DL-lactic-glycolic acid) [115], silica-polyethylene glycol hybrids [116], chitosan [117], and collagen type I have been incorporated into sol-gel coatings.

Sol-gel coatings that can release silicon compounds under in vivo conditions have been shown to promote fast and good osseointegration. For this reason, hybrid composites can be prepared through acid-catalyzed sol-gel methods using methyl-trimethoxysilane (MTMOS) and GPTMS as alkoxide precursors, which allows the degradation kinetics and Si release of the coatings to be controlled by adjusting the amount of GPTMS. Although these coatings showed osteoinduction ability in vivo, coatings with some alkoxide proportions did not demonstrate strong cellular results [118].

Another way to control the degradation profiles of HAp coatings is to incorporate silver ions, which are effective in inhibiting microbial infection [119].

For example, type I collagen layers can be assembled into a sol-gel composite coating to cover magnesium alloys such as AZ31 and ZE41 to allow the release of growing factors, enhancing cell adhesion for tissue integration. This effect is due to the high biocompatibility and cytocompatibility that type I collagen has as well as the its positive effects on cell activity [120].

Another bioactive composite coating, one composed of a silica xerogel and chitosan hybrid, was used to surface modify Ti at room temperature through a sol-gel process to obtain crack-free thin layers (<2 μm) with a chitosan content of >30 vol.%. These hybrid coatings showed bioactivity, and their properties suggested applicability to titanium-based medical implants [121].

From a biological perspective, titanium is classified as a biologically inert material that does not promote adverse reactions and is well tolerated by human tissues. However, the formation of peri-implant fibrosis may isolate the implant from the surrounding bone and induce the mobilization of prostheses, thus reducing their performance [122].

Surface hydroxy groups enhance the bioactivity of sol-gel glasses due to their promotion of calcium phosphate deposit nucleation, causing osseointegration when these materials are implanted [76].

Commercially pure (CP) Ti grade 4 substrates were dip coated with an OIH crack-free coating consisting of a sol-gel-derived $ZrO_2$−based matrix in which different PCL percentages (between 20 and 30 wt%) were incorporated. These films showed bioactivity and induced HAp formation when they were soaked in SBF. Biological evaluation with human mesenchymal stem cells (hMSCs) demonstrated that compared to pristine Ti, the coatings were nontoxic, supported cell proliferation at all compositions, and did not hamper hMSC differentiation in an osteogenic medium [122].

Although further investigation is needed to fully describe the osseointegration potential of the developed OIH, such a material may find application in the surface coatings of Ti dental implants [122].

The addition of an organic polymer such as PEG onto $SiO_2$ in a hydric composite can affect its biocompatibility and bioactivity, as cell growth and the proliferation of NIH 3T3 cells depend on the PEG amount and exposure time. The formation of a HAp layer was indeed observed on the material's surface by scanning electron microscopy (SEM)/energy-dispersive X-ray (EDX) analysis after the samples were soaked in SBF. Their effects were superior to those exerted from $SiO_2$, whose ceramics are already widely used in medical applications [123].

Homogeneous, porous and crack-free titania-based coatings can be obtained when PCL is added to a $TiO_2$ inorganic matrix to make pure grade 4 titanium (CP Ti-4) disks more bioactive, as demonstrated by the ability to induce the formation of HAp when soaked in SBF, which is a crucial property for the osseointegration of metal implants in vivo [13].

Hybrid inorganic-organic $ZrO_2$/PCL composite films showed HAp formation on their surface when the hybrid coating was exposed to SBF, implying their osteointegration ability once implanted in vivo. In addition, a WST-8 colorimetric assay shows that the coating makes Ti-4, which is generally bioinert and biocompatible [124].

Finally, it has been demonstrated that biodegradability can be controlled by adjusting the composite sol-gel hybrid coating composition, resulting in the ultimate material performance.

## 5. Conclusions

Sol-gel coatings provide excellent corrosion protection by providing a protective barrier layer for the reduced permeation of corrosive entities, providing a water repellent surface, chemically modifying the surface of a metal to make it more inert, and altering the electrical potential of surface sites. This review has presented an overview of new approaches to generate self-healing behavior in smart coatings. Extending the working life of structural and industrial metallic surfaces might depend on the fabrication of novel self-healing protective smart coatings that are able to repair scratches and eliminate corrosion. Additional development of materials with self-healing properties will reduce the loss that results from corrosion of metallic materials that are used in chemical plants, automobile parts, building structures, and home appliances.

The factors most limiting the use of sol-gel processing for coating metals are delamination, crackability, adhesion, and thickness limits. Assuring a uniform distribution on the substrate and optimizing thermal treatments (curing/drying) are crucial factors in ensuring the quality of anticorrosive coatings.

Although other processes such as plasma spraying, CVD, and electrochemical methods can be used to obtain thin film coatings of $TiO_2$, HAp or bioglass on metallic substrates for biomedical purposes, the sol-gel process has remarkable advantages over those techniques, including better control of composition, structures, and porosity, which results in greater bioactivity than materials with the same composition but prepared with other techniques. Sol-gel coatings, due to their low processing temperatures, can also be applied onto nonmetallic implant substrates, such as organic polymers such as PEEK, or nonpermanent metallic implants such as those made of magnesium alloys. In addition, the sol-gel process can perfectly enable the integration of organic polymers with an inorganic glassy matrix.

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