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Sol-Gel Films: Corrosion Protection Coating for Aluminium Alloy

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Abstract

Aluminum alloys used in aeronautical industry are susceptible to corrosion. The solution to this problem is base chromate materials, which have been heavily regulated and restricted. The development of alternatives begins in the 1970s and the 2000s, where some potential methodologies were established. The sol-gel process is one of these methods, in which thin oxide layers are deposited on the metal substrate. An important aspect is the fact of possible combinations among types of oxides and the incorporation of an organic compound to improve the performance of the films; moreover, this allows the addition of inhibitors and nanomaterials, making this method an interesting and versatile way to obtain a coating. In this chapter, we will describe the importance of the use of coating synthesized via sol-gel in the corrosion protection of metal surfaces. The advantages and disadvantages of using modified sol-gel polymer films and hybrid system coatings will also be discussed, as well as the methodologies for the chemical characterization and the feasibility of evaluating the mechanical properties of the coatings.

Keywords: sol-gel coating, aluminum alloy, hybrid, corrosion, biocorrosion

1. Introduction

The 2xxx aluminum alloys are widely used in the aircraft industry due to their high specific strength and lightweight [1]. These alloys contain elements, as copper, used to improve their mechanical properties. The presence of this element, together with others of lower content, and the history of associated thermal treatments, promotes the formation of some copper-rich

sites, known as intermetallics. Unfortunately, the heterogeneous microstructures of intermetallic make 2024 alloy become more susceptible to pitting corrosion in the media containing chloride ions, due to the formation of microscopic galvanic couples [2].

Metallic corrosion occurs because of chemical reactions between the metal surface and the environment, changing the metal over its original ore. To prevent the beginning of localized corrosion processes and to extend the service life, in the aircraft industry, the most common practice is to avoid the direct contact of the electrochemically active matrix with the surrounding environment by applying a protective coating system [3].

The traditional surface passivation treatment for aluminum alloy is conversion coating, which is produced in two steps: (i) dissolution of the base metal through reaction with the passivating solution and (ii) precipitation of insoluble compounds, a layer of corrosion product capable of resisting further chemical attack [4]. Chromate conversion coatings, typically generated from mixtures of soluble hexavalent chromium salts and chromic acid, participate in oxidation-reduction reactions with aluminum surfaces, precipitating a continuous layer of insoluble trivalent chromium and soluble hexavalent chromium compounds [5].

Corrosion protection occurs as hexavalent chromium leaches into defect sites, forming dense, insoluble trivalent chromium products. Chromate conversion coatings comparatively promote very good adhesion of organic coatings and offer as a whole system excellent corrosion protection [6]. The hexavalent chromium-containing compounds used in chromate conversion coatings are known to be carcinogenic and generally regarded as very hazardous soil and groundwater pollutants. Stricter environmental regulations have mandated the near-term removal of Cr(III)-containing compounds from corrosion inhibiting packages used for the protection of aluminum-skinned aircraft. Therefore, the need for the development of protection process exists, following nontoxic, chromium-free and environmentally friendly materials and protocols.

Several techniques are used for the deposition of coatings on metals; these methods include physical vapor deposition (PVD), chemical vapor deposition (CVD), electrochemical deposition, plasma spraying, and sol-gel process. The sol-gel process has emerged as a versatile method for preparing a host of oxide materials to protect the metal surface [7]; moreover, sol-gel materials are candidates as it is possible to form highly adherent, chemically inert films. In comparison with other deposition technologies, sol-gel technics offer several potential advantages, such as (i) preparation in room temperature, (ii) diverse and complex system, (iii) cured treatment at relative low temperature, and (iv) considered as a "green method" [8]. Thin films may be readily prepared from water-based systems, resulting in low volatile organic compound (VOC) content materials and processes. Instead, the primers and topcoats have VOC contents of 340 and 420 g/l, respectively, in comparison with the aqueous sol-gel solutions suitable for spray coating on aluminum substrates, which have a VOC content of 100–200 g/l [9]. On the other hand, the method allows to obtain thin films of sub-micrometer thickness with high purity in multiple combinations. By forming dense coatings, sol-gel films act as barriers for diffusion of aggressive species, such as chlorine and oxygen, blocking the electron transfer of metal surface to and from the environment. Moreover, the flexibility of the sol-gel process also permits the incorporation of corrosion inhibiting compounds, thereby providing another mechanism for corrosion protection. These characteristics lead to the possibility of forming

environmentally compliant coatings capable of improving corrosion resistance without the use of metal chromates or the generation of liquid hazardous waste products [6].

The anticorrosion behavior of coating is studied using electrochemical methods, which allow to obtain the susceptibility of metal to be corroded. The most important technics used are polarization curves and electrochemical impedance spectroscopy.

In the following topics, we will describe the methodology to obtain coating from oxide species using sol-gel technics. Moreover, the diversity and complex system of hybrid coating will be reviewed. In this way, the advantages and disadvantages of using modified sol-gel polymer films for the generation of smart coatings will be discussed also. Finally, the chemical characterization and the feasibility of evaluating the mechanical properties of the coatings will be analyzed as well.

2. Synthesis and deposition of sol-gel coatings

The sol-gel process can be described as the evolution of an oxide network by continuous condensation reactions of molecular precursors in a liquid medium [10]. Two ways to prepare sol-gel coating have been proposed: the inorganic method and the organic method. The inorganic method involves the evolution of networks through the formation of a colloidal suspension (usually oxides) and gelation of the sol (colloidal suspension of very small particles (1–100 nm)) to form a network in continuous liquid phase. But the most widely used method is the organic approach, which generally starts with a solution of metal/metalloid alkoxide precursors, M(OR)n, in an alcohol or other low molecular weight organic solvent, where M can represent different elements such as Si, Ti, Zr, Al, Fe, B, etc. and R is typically an alkyl/allyl group. Sol-gel processing proceeds in several steps which will be discussed later: (i) hydrolysis and condensation of the molecular precursors and formation of sols, (ii) gelation (sol-gel transition), (iii) aging, and (iv) drying [11].

2.1. Hydrolysis and condensation

In the sol-gel process, hydrolysis and condensation are equilibrium reactions and can proceed simultaneously once the hydrolysis reaction has initiated. The reaction mechanisms for acid or base catalysis are very different and have to be considered separately [12]. The pH is an especially important parameter to control the morphology of coatings. At intermediate pH, the reaction rate of condensation is proportional to the concentration of the OH^- ions. At pH lower than about 2, the silicic acid species are positively charged, and the reaction rate of the condensation is proportional to the concentration of H^+. While under strong alkaline conditions, the solutions contain mainly anionic species. For this reason, the rate of Si—O—Si cleavage or redissolution of particles is high at alkaline pH.

Under acidic conditions, the oxygen atom of a $\equiv$Si—O$^-$, $\equiv$Si—OH, or $\equiv$Si—OR group is protonated in a rapid first step. A good leaving group (water or alcohol) is thus created. In addition, electron density is withdrawn from the central silicon atom, rendering it more electrophilic and thus more susceptible to attack by water (in hydrolysis reactions) or silanol groups (in condensation reactions).
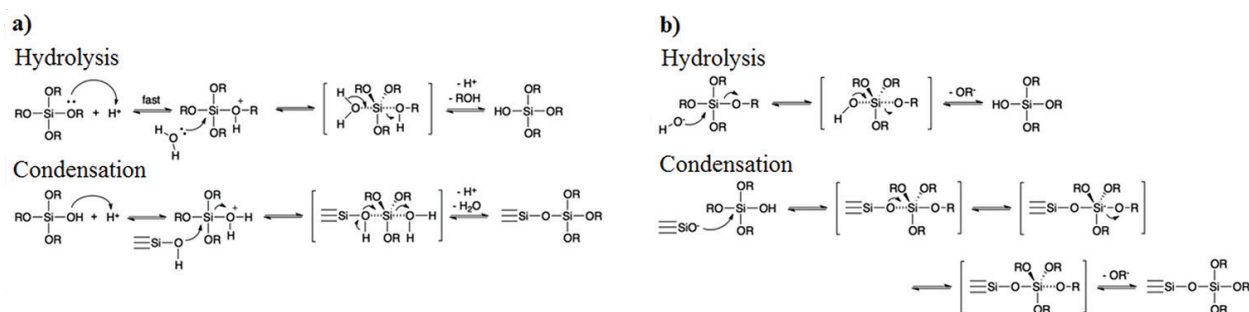
Figure 1. General mechanisms of synthesis sol-gel catalyzed (a) acid, and (b) base conditions.

Under basic conditions (**Figure 1**), the reaction proceeds by nucleophilic attack of either an OH^- (in hydrolysis reactions) or a $\equiv Si\!-\!O^-$ ion (in condensation reactions) to the silicon atom with an SN_2-type mechanism. The entering OH^- or $\equiv Si\!-\!O^-$ group is formed by deprotonation of water or a $\equiv Si\!-\!OH$ group. Under strong alkaline conditions, the $Si\!-\!O\!-\!Si$ bonds can be cleaved again by OH^-. Inductive effects of the substituents attached to a silicon atom are very important, because they stabilize or destabilize the transition states or intermediates during hydrolysis and condensation. The electron density at the silicon atom decreases in the following order: $\equiv Si\!-\!R` > \equiv Si\!-\!OR > \equiv Si\!-\!OH > \equiv Si\!-\!O\!-\!Si$.

For acid catalysis, the electron density at the silicon atom should be high since the positive charge of the transition state is then stabilized better. Therefore, the reaction rates for hydrolysis and condensation under acidic conditions increase in the same order as the electron density. For base catalysis, a negatively charged intermediate must be stabilized.

Therefore, the reaction rates for hydrolysis and condensation increase in the reverse order of the electron density.

2.1.1. Gelation, aging, and drying

During the gelation, the colloidal particles and condensed species link together to become a three-dimensional network and the viscosity increases sharply. Physical characteristics of the gel network will depend greatly upon the size of particles and extent of cross-linking prior to gelation [13]. Aging of the prepared sol-gel prior to application on the metallic substrate also affects strongly the corrosion protection properties of the resulting coatings. Aging of the sol can promote the condensation reactions of the precursors, including formation of further crosslinks and increasing the viscosity of the sol-gel, which can eventually lead to the formation of thick coating with a high defect density [14]. During drying, loss of water, alcohol, and other volatile components takes place. The evaporation of the liquid from a wet gel generally proceeds in more than one stage, where the liquids flow through the polymer evolving to a stable rigid condition, and where the effect of the surface tension on the mechanical properties of the final coating, is also considered [15].

Two processes are important for the collapse of the network. First, the slower shrinkage of the network in the interior of the gel body results in a pressure gradient that causes crack. Second, larger pores will empty faster than smaller pores during drying; that is, if pores with different

radii are present, the meniscus of the liquid drops faster in larger pores. The wall between pores of different sizes is therefore subjected to uneven stress and crack. Low-temperature drying is normally employed for drying of hybrid sol-gel coatings entrapping organic compounds. Although compact crack-free films can be obtained, room temperature cured sol-gel coatings exhibit higher water sensitivity compared to those cured at higher temperatures. Higher cure temperatures (up to 200°C) promoting condensation reactions and formation of dense hybrid coating improve the barrier properties. By controlling the aging and drying conditions, further pore size and mechanical strength control may be achieved.

Despite the fact that the most used alkoxides are the silicon-type in sol-gel coating synthesis, it is pertinent to make a brief mention about the transition metal alkoxides.

There are two important differences between silicon and transition metal alkoxides that have to be considered when we want to synthesize a sol-gel coating [16]: (i) metals are more electropositive (Lewis acidic) than silicon and therefore more susceptible to a nucleophilic attack and (ii) the preferred coordination number is higher than their valence. The increase of the coordination number beyond the valence is reached by interaction with any nucleophilic (Lewis basic) entity in the system. When we compare SiO_2 and TiO_2, both central atoms are in the IV oxidation state. However, silicon is always four coordinated (tetrahedral SiO_4 building blocks) while titanium in rutile is six coordinated (octahedral TiO_6 building blocks). The mechanisms of condensation reactions of metal alkoxides are similar to those of silicon alkoxides in a sense that an M—OH group undergoes nucleophilic attack by another metal atom. Due to the higher propensity of metal atoms to interact with nucleophilic agents, base or acid catalysts are not needed in most cases.

When a silica network grows, the question that decides the morphology of the obtained coating is whether condensation occurs preferentially at the end of chain of corner sharing SiO_4 tetrahedra or at a central atom. For transition metals, this issue is more complicated and hardly understood in detail in most cases. An additional difference between metal alkoxide and silicon alkoxide-driven sol-gel process is the morphology of the final material. While in the silicon-based sol-gel process only amorphous materials are produced, the metal alkoxides can form crystalline compounds.

2.1.2. Considerations

Two points are considered by the time of synthesis of sol-gel coating, alkoxy group/H_2O ratio (Rw) and solvent. Alkoxides are employed as precursors for the sol-gel process, as mentioned above. In the case of silicon, the most prominent alkoxides are tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS) (**Figure 2**) [10]. Both precursors are liquid under standard conditions, and TMOS shows a faster hydrolysis reaction compared to TEOS but, at the same time, generates methanol, which is avoided for its toxicity. The application of these precursors in the sol-gel process would lead to a three-dimensional network and finally, after heating, to a coating. Considering that alkoxides must first be hydrolyzed before condensation reactions can take place, the hydrolysis rates of alkoxysilanes are influenced by both the inductive effects and steric factors. Any branching of the alkoxo group or increasing of the chain length lowers the hydrolysis rate of the alkoxysilanes. It means that the reaction rate decreases in the order $Si(OMe)_4 > Si(OEt)_4 > Si(O``Pr)_4 > Si(O`Pr)_4$.
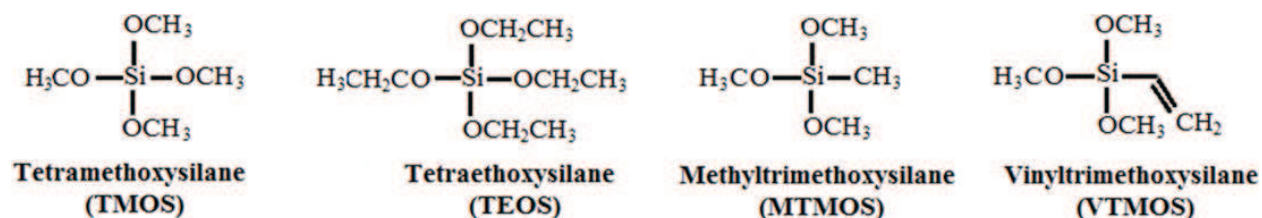
Figure 2. Examples of some precursors commonly used in sol-gel coatings.

The overall reaction for sol-gel processing of tetraalkoxysilanes implies that two equivalents of water (Rw = 2) are needed to covert $Si(OR)_4$ if no condensation takes place. Increasing the water proportion generally favors the formation of silanol groups over Si—O—Si groups. The Rw, together with the kind of catalyst, strongly influences the properties of the silica gels [17].

A solvent may be necessary to homogenize the reaction mixture of alkoxide-based systems, especially at the beginning of the reaction. Polarity, dipole moment, viscosity, and protic or non-protic behavior of the solvent influence the reaction rates and thus the structure of the sol-gel coating. Polar and particularly protic solvents (H_2O, alcohols, etc.) stabilize polar species such as $(Si(OR)_x(OH)_y)n$ by hydrogen bridges. The latter generally play a very important role in sol-gel systems. Nonpolar solvents (dioxane and tetrahydrofuran) are sometimes used for organotrialkoxysilanes ($R`Si(OR)_3$) or incompletely hydrolyzed alkoxide systems [17].

2.2. Application techniques of the sol-gel coatings

A sol-gel coating can be applied to a metal substrate through various techniques, such as dip coating and spin coating, which are the two most commonly used coating methods. Spraying [18] and electrodeposition [19] also emerged recently and could be the major sol-gel coating application methods in the future. In both methods, spin coating and dip coating, the sol-gel is directly deposited onto the support. The condensation reaction can also occur between silanol and hydroxyl groups of the metal (obtained by the activation of the surface with bases), leading to the covalent bonding of silane to the surface: —SiOH + HO-surface → —Si—O-surface + H_2O (1).

It is generally accepted that during the sol-gel process, the sol precursor first hydrolyzes, and then, the hydrolyzed species are adsorbed onto the surface undergoing cross-linking to form a continuous film.

2.2.1. Spin and dip coating

The production of thin films by spin coating was initially reported by Ogawa in the 1996 [20]. Among other techniques, spin coating is the most easily applicable one for obtaining uniform thin layers on flat surfaces [21]. Experimentally, a small amount of the coating material is deposited onto the center of the support. Subsequently, the support is rotated at high speed in order to spread the coating material by the centrifugal force. In general, the higher the rotation speed, the thinner the film. Therefore, by selecting the appropriate spin rate, it is possible to modulate the film thickness [21].

Besides the very interesting results obtained and the very good performances of this simple deposition technique, spin coating possesses some drawbacks concerning the size and shape of the substrates. In fact, as reported by Tyona [22], large supports are difficult to be homogeneously deposited by this method. Additionally, in a typical spin-coating deposition, minority of the 5% of the starting solution is deposited successfully onto the substrate forming the thin film, whereas the complement percentage is lost due to the rotation of the spinner. Further, the final morphology of the coated substrate can be influenced by several parameters such as spin speed, time of spin, acceleration, fume exhaust, etc.

Dip coating is one of the most convenient methods used in the laboratory and industry to deposit films onto a metallic surface with a controlled thickness from a sol-gel solution. This method is simple and provides excellent reproducibility [23]. Basically, the method may be separated into three important stages: (1) *Immersion and dwell time*: The substrate is immersed into the precursor solution at a constant speed followed by a certain dwell time in order to leave sufficient interaction time of the substrate with the coating solution for complete wetting. (2) *Deposition and drainage*: By pulling the substrate upward at a constant speed, a thin layer of precursor solution is entrained. Excess liquid will drain from the surface. (3) *Evaporation*: The solvent evaporates from the fluid, forming the as-deposited thin film, which can be promoted by heated drying. Subsequently the coating may be subjected to further heat treatment to obtain a more dense film [10].

2.2.2. Electrochemical deposition

The electrochemical deposition of sol-gel films provides an alternative for shifting the pH on the substrate. In aerated aqueous media, it is well known that by applying cathodic potential, the following reactions occur at the electrode surface:

$$O_2 + 2\,H_2O + 4e \;\rightarrow\; 4\,OH^- \tag{1}$$

$$2\,H_2O + 2e \;\rightarrow\; 2\,OH^- + H_2 \tag{2}$$
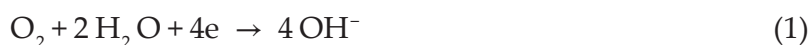
Both reactions generate OH^- ions that increase the interfacial pH near the cathode, which catalyzes the sol-gel process facilitating the film formation. There are three advantages of electrodeposition technic: (1) pH varies only close to the cathode, so the stability of the bulk solution is not affected, (2) the deposition process is controllable by electrochemical parameters, and (3) the film deposition is restricted to the conducting part of the surface and controlled by the kinetics of the electrochemical process [24].

2.3. Hybrid organic-inorganic sol-gel coatings

In order to overcome the limitations associated with conventional inorganic sol-gel coatings, such as brittle oxide films, thicker coatings (>1 μm), crack-free, and relatively high temperatures (400–800°C), the hybrid coatings by the incorporation of organic groups in the inorganic sol-gel network have shown good results [24].

Two different approaches can be used for the incorporation of organic groups into an inorganic network by sol-gel processing, namely, embedding of organic molecules into gels without chemical bonding (class I hybrid materials) and incorporation of organic groups through covalent bonding to the gel network (class II hybrid materials). Embedding of organic molecules is achieved by dissolving them in the precursor solution. The gel matrix is formed around them and traps them, and the organic and inorganic entities interact only weakly with each other. The inorganic network and the organic network interpenetrate but are not bonded to each other [14]. Despite the presence of weak dispersion forces and Van der Waals interactions between organic and inorganic components of such hybrids, the physical bonds are not stable enough for long-term applications involving weathering. Formation of strong covalent bonds between organic and inorganic components can significantly improve corrosion protective properties of the hybrid coatings. Very important sol-gel materials are obtained when functional or nonfunctional organic groups are covalently linked to oxide networks (class II hybrid materials). Silicate hybrids are mostly done by using organotrialkoxysilanes, $R`Si(OR)_3$, as precursors to sol-gel processing. Nearly any organic group $R`$ can be employed; the only requirement is that the group $R`$ must be hydrolytically stable. Since Si—C bonds are hydrolytically stable, the organic groups are retained in the final material after sol-gel processing.

Different functional groups impart different corrosion protective properties to hybrid coatings. Moreover, the corrosion protective properties of the hybrid coatings dramatically depend on the presence, the type, and the number of the reactive groups of the used agent. For this reason, organotrialkoxysilanes are typically copolymerized with tetraalkoxysilanes or metal alkoxides to obtain the properties characteristic of highly cross-linked networks. This allows incorporation of organic groups without lowering the network connectivity because one Si—O—Si entity is replaced by Si—R``—Si. The groups $R``$ can range from simple alkylene or arylene groups to more complex entities. The hybrid sol-gel coatings containing functional groups show a higher cross-link density and better mechanical properties [25]. Not only the nature of organic components but also their content in the hybrid sol-gels plays a very important role in the final properties of the hybrid coatings. An increase in the organic content of the hybrid coatings leads to the formation of less porous and thicker films appropriate for barrier protection of metals. However, a high concentration of organic component can lower the adhesion and the mechanical properties of the final coating. So it is important to point out that there is an optimum ratio for inorganic-organic components to deliver maximum corrosion resistance. The optimum organic/inorganic ratio varies depending on the precursors employed and on the coating application technique [26]. Hydrophobic hybrid coatings can reduce the kinetics of the corrosion processes by delaying penetration of water and other electrolytes toward the metal/coating interface. However, a prolonged exposure of the hybrid coatings to water/electrolyte will eventually result in moisture penetration of the metal/coating interface. Considering the reversible nature of hydrolysis and condensation reactions involved in the creation of the coating, water penetration can promote hydrolysis of the bonds formed during condensation reaction resulting in delamination [27]. The final film can carry specific organic functions, which can present certain properties, such as good adhesion, self-healing, abrasion resistance, scratch resistance, hydrophobicity, etc. Network formation is only possible if the precursor used has at least three possible cross-linking sites. Both, tetraalkoxysilanes $Si(OR)_4$ and trialkoxysilanes $(RO)_3SiR'$, possess this ability.

2.3.1. Sol-gel coatings synthesized in the presence of a performed polymer

This route of synthesis means that the polymer is mixed with the precursors and hydrolysis and condensation are started [28]. It is important to determine the best reaction conditions to avoid phase's separation. Therefore, the right choice of solvent is of major significance. Typical polymer solvents depending on the functional groups and polarity of the polymers are tetrahydrofuran (THF), dimethoxyethane (DME), alcohols (methanol, ethanol, isopropanol, etc.), acetic acid, etc. During sol-gel reaction, alcohols are liberated which can change the solvent properties resulting to precipitation of the initially soluble polymers, leading to heterogeneous films. Therefore, the choice of the polymer and solvent is important in this synthetic route. Polymers with functional groups can interact with the sol-gel structures, for example, by hydrogen bonding, such as alcohols or amines. In many cases, an effective interaction between the polymer and the inorganic structure results in a homogeneous distribution of small inorganic structures in the polymer matrix.

2.4. Doping of the sol-gel coatings

Despite the effective barrier protection of metallic substrates by hybrid sol-gel coatings, these systems are prone to fail because of water ingress into the films. For this reason, incorporation of active species such as binding agents and corrosion inhibitors, which add active protection mechanisms to the system, can improve the protective properties of the hybrid sol-gel coatings. Thus, incorporation of nanoparticles such as silica, ceria, zirconia, alumina, titania, and zeolite, as mechanical reinforcement, were the first proposed approaches for modification of hybrid sol-gel coatings [29]. The improved mechanical properties, increased thickness, and lower crack sensitivity achieved by addition of a controlled amount of the particles resulted in enhanced corrosion protection of the underlying substrate. However, the particle size and surface modification have shown to be critical, as agglomeration of the embedded particles promoted by gelation process could lead to coating rupture and deterioration of the coating barrier properties [14]. It is important to point out that the critical dopant concentration, which physical/mechanical properties in the coating starts to degrade, must always be considered. Moreover, a strong interaction between particle and matrix interfaces is required. Corrosion inhibitors can either be added (i) directly to the coating formulation or (ii) immobilized in carriers to reduce the possible interactions with the matrix and control release of the inhibitor [30]. In addition, nanoparticles not only can be added but also can be formed in situ in the coatings, eliminating some of the challenges associated with the strong interfacial forces between matrix and particles [31].

2.4.1. Direct and indirect addition of inhibitors

The most common way of inclusion of corrosion inhibitors into sol-gel systems is mixing them with the coating formulation [32]. The most important factor to be considered in such systems is the solubility of inhibitor in the corrosive media. While a low solubility of inhibitor can lead to a weak self-healing effect due to the low concentration of active agents at damaged site, a high solubility will limit prolonged healing effect because of rapid leach out of the active agents from coating, producing the coating degradation by blistering and delamination. Despite the potential drawback of this class of extrinsic self-healing sol-gel coatings,

they have been extensively studied for protection of different metallic substrates due to ease of preparation. The corrosion inhibitors used can be divided according to their nature into (i) inorganic and (ii) organic inhibitors [33]. Some of the most used inorganic inhibitors are the rare earth metals and some transition metals such as Ce, La, and Zr which have showed an improved anticorrosive performance in the doped hybrid coatings compared to the undoped ones [34]. Incorporation of the active Ce ions not only facilitates preparation of dense and defect-free hybrid coatings but also increases the protection mechanism via selective leaching of Ce ions to the damage site restoring the coating's protective properties [35]. Organic inhibitors prevent corrosion by either increasing the anodic or cathodic polarization resistance of the corrosion cell or retarding diffusion of corrosive agents to the metallic surface [36]. However, their inhibition efficiency depends on the chemical composition, molecular structure, and affinity of the metal surface. Organic inhibitors such as phosphonic acid, 2-mercaptobenzothiazole (MBT), 2-mercaptobenzimidazole (MBI), benzotriazole (BTA), etc. have been successfully incorporated into sol-gel systems to improve their corrosion protection properties by inducing active protection [37]. In several cases, release of organic molecular species from the hybrid sol-gel matrix is based on a pH-triggered release mechanism. With this method, it is possible to release inhibitors only at damaged areas due to local pH changes.

Although incorporation of corrosion inhibitors into sol-gel coatings is a promising route in the development of active corrosion protective hybrid coatings, there are inevitable drawbacks associated with direct mixing of active agents into coating formulation. Firstly, it is quite difficult to control leach out of entrapped inhibitors especially when they are poorly soluble within the coating matrix. Secondly, inhibitors can chemically interact with the coating matrix losing their own activity and lowering the barrier properties of the matrix. A probable solution to this problem is the encapsulation of active species or complexing them with other chemicals [38]. A quite simple approach for inhibitor entrapment/immobilization is based on the complexation of organic molecules with β-cyclodextrin. Cyclodextrins are cyclic oligosaccharides that possess a unique molecular cup-shaped structure with a hydrophilic exterior and a hydrophobic interior cavity. They are able to form complexes with various organic guest molecules which fit within their cavities. Organic aromatic and heterocyclic compounds are normally the main candidates for the inclusion complexation reaction. 2-Mercaptobenzothiazole (MBT) and 2-mercaptobenzimidazole (MBI) were successfully loaded in β-cyclodextrin [33]. In the case of cyclodextrin complexes, incorporation of the inhibitor-loaded particles in sol-gel coatings has been more efficient than direct inhibitor loading in imparting long-term self-healing function. On the other hand, ceramic particles such as silica and alumina can be employed as micro-/nano-containers to immobilize corrosion inhibitors. The selected inhibitors can be entrapped on the carriers through controlled hydrolysis of the relevant precursors in the inhibitor-containing aqueous solutions [39].

3. Physical-chemical characterization

The proposal of this topic is to show an overview of some methodologies of characterization in order to understand the information related to properties of film coating. The most useful

and used technics to characterize the sol-gel coating are infrared spectroscopy (IR), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM).

3.1. Infrared spectroscopy (IR)

Infrared spectroscopy is based on the vibrations of atoms of a molecule. An IR spectrum is obtained by passing an IR radiation through a sample and determining what fraction of the incident radiation is absorbed at determinate energy. The energy at which any peak in an absorption spectrum appears corresponds to the frequency of a vibration of a part of a sample molecule. The interactions of IR radiation with matter may be understood in terms of changes in molecular dipoles associated with vibrations and rotations [40].

IR technic allows characterize bonds Si—O, Si—Si, and Si—C. Furthermore, this analysis is used to determine the presence of active molecules in hybrid sol-gel film which has been modified using, among others, organic substituent such as hydrocarbon chain (C—H, C—C) [41], organic compound [42], and inhibitor [43].

3.2. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy is an established quantitative method for the determination of elemental abundance and the assessment of chemical binding [44]. Photoelectron production in its simplest form describes a single-step process in which an electron initially bound to an atom/ion is ejected by a photon. Since photons are a massless (zero rest mass), charge less package of energy, these are annihilated during photon-electron interaction with complete energy transfer occurring. The general equation for this process is $hv = BE + KE + \varphi_{spec}$. If this energy is sufficient, it will result in the emission of the electron from the atom/ion as well as the solid. The kinetic energy (KE) that remains on the emitted electron is the quantity measured. This is useful since this is of a discrete nature and is a function of the electron binding energy (BE), which, in turn, is element and environment specific, and $\varphi spec$ is the work function of the electron spectrometer, which is usually quite small (< 5 eV) compared to BE and KE [45]. It is convenient in surface analysis to measure BE and KE with respect to the Fermi level. Since the binding energies of core electrons are different in different atoms, XPS is capable to identify the elemental compositions of materials by measuring the KEs of their ejected electrons. XPS can detect all the elements except for H and He. In addition, XPS is sensitive to the chemical environments of the atoms it detects.

The popularity of XPS stems from its ability to: (a) Identify and quantify the elemental composition of the outer 10 nm or less of any solid surface with all elements from Li-U detectable. Note: This is on the assumption that the element of interest exists at >0.05 atomic %. (b) Reveal the chemical environment where the respective element exists in, that is, the speciation of the respective elements observed. (c) Obtain the information above with relative ease and minimal sample preparation [45].

In this way, the XPS help in the analysis of sol-gel coating in order to determine the oxide state of doped polymer [46], the presence of metal [47], and the bond between metal and polymer [6].

3.3. Scanning electron microscopy (SEM)

A basic SEM consists of an electron gun (field emission type or others) that produces the electron beams; electromagnetic optics guide the beam and focus it. The detectors collect the electrons that come from the sample (either direct scattering or emitted from the sample), and the energy of the detected electron together with their intensity (number density) and location of emission is used to put the image together. SEM also offer energy dispersive photon detectors that provide analysis of X-rays that are emitted from the specimen due to the interactions of incident electrons with the atoms of the sample [48].

SEM technic allows to characterize the coated metallic surface [49] and determine the thickness of deposited polymer [41].

4. Mechanical characterization

The properties of sol-gel coatings have a strong dependence on the substrate on which they have been generated. The requirements for the coating vary depending on the type of substrate, ranging from purely physical (e.g., optical properties), through chemical (e.g., anti-corrosion properties), to purely mechanical (e.g., resistance to wear). The type of coating generated is a direct function of the desired final properties, being able to choose between inorganic coatings or hybrid coatings (organic-inorganic).

The main qualities required of any coating generated on a metallic substrate, regardless of its application in service, are:

- Homogeneity of the thickness of the obtained coating

- Homogeneity in the chemical composition of the coating, to present the same mechanical behavior throughout the sample

- High adhesion to the substrate, guaranteeing structural and mechanical stability over time

The first two requirements are easily achievable with sol-gel coatings. Regarding the adhesion, ceramic coatings obtained following the sol-gel route present a high adhesion to the metallic substrates due to the presence of hydroxyl radicals (─OH) on the surface of the latter which manage to form a chemical bond between atoms of the deposited *gel* and atoms of the outer surface of the substrate.

Aluminum alloy substrates have been coated with sol-gel to improve their corrosion behavior, using mainly alloys with aeronautical or automotive applications, as well as structural interest in the civil field. The surface preparation of the substrates to be coated is usually initiated with chemical degreasing. Subsequently, the substrate can be simply coated, or it can be subjected to the generation of a certain roughness by roughing or polishing. The coating generated by the sol-gel route can be the only protection system, or it can be used in combination with other systems, such as special paint for aeronautical applications.

The main characteristics of the sol-gel coatings on aeronautical aluminum alloys are anticorrosive and mechanical together with wear behavior.

García-Heras et al. [50] demonstrate the importance of the surface preparation of the substrate and the concentration of alkoxide precursor in the anticorrosive efficiency of silica coatings manufactured on the 2024 T6 aluminum alloy. Hamdy and Butt [51] demonstrate the effectiveness against corrosion of inorganic silica coatings, starting from TEOS as a precursor, on the 6063 aluminum alloy without anodizing and anodizing prior to deposition, as well as the influence of the treatment thermal densification. It has been reported that the use of hybrid coatings generates, on the one hand, greater coating thicknesses, and in addition, a very adherent surface is formed for the subsequent painting system on the 2024 alloy [52]. The same degree of protection as by coating and painting systems has been achieved by Liu et al. [53]. An alternative way of generating hybrid coatings is by adding inorganic particles to sol solutions of alkoxides with non-hydrolyzable groups [54], although the percentage of added particles must be optimized, since an excess means the formation of thicker coatings but with pores, favoring the formation of pitting corrosion. The amount of inorganic particles added to the sol-gel is not the only determining factor to obtain a good behavior against corrosion, since hydrophobic particles generate greater resistance to corrosion than hydrophilic particles [55].

It should be noted that hybrid coatings have greater thickness than inorganic coatings, so their effectiveness against corrosion is usually greater. The greater thickness of these coatings is due to the presence of residual internal porosity, generated by the non-hydrolyzable organic groups of the structural network of the coating [56]. These pores are closed and are not detrimental to the anticorrosive behavior of the coating, although they do significantly reduce their mechanical behavior.

Currently, it is sought that the sol-gel coatings on aluminum alloys, in addition to having a good corrosion behavior, also have a good mechanical behavior. The mechanical properties of the coatings made by the sol-gel route are not easy to determine; the modulus of elasticity, the hardness, the adhesion of the coatings to the metallic substrates, and the tribological properties (wear) are the main properties that have been evaluated in this type of coatings.

4.1. Mechanical properties: determination of modulus of elasticity, hardness, and fracture toughness of coatings

Parameters such as modulus of elasticity (E), hardness (H), or fracture toughness must be known to anticipate the in-service performance of such coatings. The most used technique for the determination of the modulus of elasticity of materials is the tensile test, which is not applicable to characterize a coating. The coatings generated by sol-gel have thickness in the order of microns, so that the usual techniques of characterization of the hardness of the materials, hardness or microhardness, apply too much load to the coatings, obtaining the mechanical response of the substrate also. The main obstacle that exists when knowing the mechanical properties of the coatings by hardness tests is to avoid the influence of the substrate on the results of the test, which leads to perform tests at micro- or nanometric scale, depending on the thickness of the covering.

The microhardness test instruments (micro-durometers) do not allow to apply forces small enough to provide penetrations of the order of 10% of the thickness of the coating, necessary to avoid the influence of the substrate in the measurements made, an essential factor when the coating has small thickness. In addition, the durometers base the determination of the hardness in the measurement of the size of the residual footprint left by the penetrator on the surface tested, but at such a low load, to achieve low penetration, this residual trace cannot be determined with sufficient accuracy as to provide acceptable hardness values. As an example, the uncertainty associated with the determination, by conventional optical methods, of a diagonal measuring 5 µm corresponding to the residual footprint made with Vickers indenter is of the order of 20%. This uncertainty increases as the size of the diagonal decreases, being able to reach 100% for a size of 1 µm.

This leads to the need of developing new mechanical characterization techniques for thin coatings. Among them the most used, and that allows the determination of both E and H, is nanoindentation. The nanoindentation technique overcomes the limitation of the measurement of the size of the footprint basing the determination of the hardness (H) and the modulus of elasticity (E) of the material in continuous measurement of the depth of penetration and the known geometry of the indentator.

In this technique, the applied load displacement curve inside the material is recorded continuously. In the initial part of the load cycle, at low applied load, the tested material elastically deforms, to become plastically deformed at higher loads. If the plasticization of the material has taken place during the loading process, the load-displacement data of the discharge branch are different from those of the load branch. In this way, a trace is generated on the surface of the material tested, because the plastic deformation generated has not been recovered, only the elastic deformation. The Berkovich indentator is the one commonly used in nanoindentation tests, because it has a three-sided pyramid geometry in which it is easier to achieve a point vertex than with a four-sided pyramid (Vickers), allowing better control of the process of indentation.

The nanoindentation tests in this type of coatings are generally carried out by means of a nanoindentation module coupled to an AFM equipment, avoiding the mechanical response of the substrate. This allows having the resolution of the AFM in the horizontal and vertical displacement and therefore carrying out the tests in the selected areas with high precision.

The mechanical properties of the coating, as well as its resistance to corrosion, are also modified by the densification temperature used, since it conditions the microstructure of the obtained coating, being able to go from an amorphous state to a crystalline state. Olonfinjama and collaborators [57] proved the improvement of the mechanical properties obtained in mononane and multilayer titania coatings with crystalline microstructure (densification at 500°C) deposited on metal substrates, with respect to obtaining amorphous microstructure (densification at room temperature). The results obtained by nanoindentation at very low load show that the obtaining of crystalline coatings implies a 25% increase in the hardness of the coating (1.5 GPa) and an increase of approximately 40% of the modulus of elasticity (85 GPa) with respect to the coating values in the amorphous state. This shows that by means of the heat treatment at high temperature, the coating has gone from an

amorphous initial state to a crystalline structure, beneficial for the mechanical performance of the coating. The influence of the thickness of the coatings in the mechanical properties of these is null.

By means of thermal treatments at a high-temperature furnace, the densification of the coatings is achieved, although there are other ways to achieve this densification. The influence of the densification technique on the mechanical properties of the coating is evident in the research carried out by Jämting et al. [58], which densify titania sol-gel coatings by bombardment with hydrogen ions and by heating in an oven. The nanoindentation technique demonstrates that by bombardment the highest densifications are obtained in the coating in contact with the substrate, while densifying in the furnace the greater densifications of the coating is achieved in the surface area. The time used in the densification also modifies the mechanical properties of the coating, as Lucca et al. [59] confirm in zirconia coatings made by sol-gel and coatings by immersion on metal substrates.

The nanoindentation technique was also used to calculate the fracture toughness of coatings [60], since the load-displacement curves obtained from the tests make it possible to determine the load at which the coating cracks.

Mammeri et al. [61] investigated the mechanical properties of hybrid silica coatings by nanoindentation, demonstrating that the test discharge curve does not reflect only the elastic properties of the coating but shows the creep induced by the response of the polymeric zones of the coating. Therefore, the time in which the discharge is performed must be designed to avoid this temporary response of the coating as much as possible, making a series of corrections [62] for the calculation of the modulus of elasticity and the hardness of the material.

A novel way of obtaining and densifying sol-gel coatings are by using the laser technique [63] with which coatings with high values of E and H are obtained, possibly due to the refinement by laser densification of the structure of the obtained coatings.

4.2. Adherence: determination of the adhesion of coatings

The usual techniques for determining the adhesion of coatings such as three-point bending techniques or the technique of peeling with adhesive tapes lose effectiveness when evaluating the adhesion of fine ceramic coatings. This is normally because the failure of these coatings is due to cracking, since they are fragile coatings.

Techniques such as nanoindentation or nanoray are being used to determine the adhesion of this type of coatings, including coatings obtained by sol-gel. In nanoindentation tests, cracking at the interface is detected in the load-displacement curve since a change in slope occurs during the loading process. By means of the nanoray tests, in which the normal load applied to the material increases while the indenter moves over the surface of a series of microns, the loads can be detected at which the separation between coating and substrate occurs, either by acoustic methods, by sudden increase in the coefficient of friction, or by the subsequent observation of the scratching track.

The surface roughness of the substrate and the densification temperature of the coating are factors that influence the adherence of the coatings. Xie and Hawthorne [64] show that the adhesion of the sol-gel coatings increases with increasing surface roughness of the substrates and the densification temperature. When the generated sol-gel coating is hybrid, increasing the proportion of the non-hydrolyzable alkoxide increases the adhesion of the coating to the substrate [65].

Another way to determine the adhesion between coating and substrate is the use of traction tests on pieces joined to a simple overlap using an epoxy base adhesive.

4.3. Tribological properties: weathering

So that the coating can be used in anti-wear applications, it must have thicknesses between 0, 5, and 10 µm, with which multilayer systems are used when the sol-gel route is chosen to manufacture the said coatings. Normally, high temperatures are used for the densification of the coating, so it can meet the anti-wear requirements [65]. The temperature must be selected considering that the mechanical properties of the substrate do not decrease. This is especially important when working with substrates of aluminum alloys, since the temperatures at which this change in properties occurs are much lower than in the case of titanium alloys or carbon steels. The densification temperatures influence the final structure of the coating. Thus, high temperatures tend to form crystalline coatings, while low temperatures tend to form amorphous coatings.

Sol-gel coatings for anti-wear applications are usually fundamentally inorganic, with the most common being those of alumina, zirconia, or silica. The use of hybrid coatings is less widespread, due to the mechanical limitations that often appear in these coatings because of their high percentage of porosity. However, the use of modified inorganic coatings is extended, either by the addition of lubricating particles that reduce the coefficients of friction or by the addition of organic modifiers to the starting sol that generate a decrease in the roughness of the coating.

Taktak and Baspinar [66] demonstrated an augment of the wear resistance by increasing the crystalline and decreasing of the coefficient of friction. These effects were explained based on two concepts: First, the presence of crystalline phase in an amorphous matrix prevents the propagation of cracks originated during the wear process, due to the presence of crystalline grain boundaries [67]. The presence of crystalline phase in an amorphous matrix increases the strength and the fracture tenacity of the material, due to the compression stresses that the said phase generates [68].

The doping of hard coatings is another of the widely ways used to improve their mechanical or tribological properties [69].

A typical way to evaluate the wear behavior of the coating is through *pin-on-disc* tests without lubrication and at room temperature. Once the tests have been carried out, the wear tracks are observed by means of SEM in order to correlate the values obtained after the tests with the morphology of the wear tracks.

5. Conclusions

The coating obtained using sol-gel processing has shown good performance as corrosion barrier in the protection of metal substrate. The versatility along with the "green" methodology makes this process an excellent alternative to replace the conventional coating.

The hybrid polymer improves the mechanical properties and allows a better control in the preparation of coat. Moreover, the process to obtain the polymer allows the incorporation of organic and inorganic compounds. Thus, considering these points, the effort of the scientific community is obtaining a "smart coating," which present multiple properties.

Acknowledgements

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