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REVIEW PAPER

Organic–inorganic hybrid sol–gel coatings for metal corrosion protection: a review of recent progress

R. B. Figueira, C. J. R. Silva, E. V. Pereira

Abstract This paper is a review of the most recent and relevant achievements (from 2001 to 2013) on the development of organic–inorganic hybrid (OIH) coatings produced by sol–gel-derived methods to improve resistance to oxidation/corrosion of different metallic substrates and their alloys. This review is focused on the research of OIH coatings based on siloxanes using the sol–gel process conducted at an academic level and aims to summarize the materials developed and identify perspectives for further research. The fundamentals of sol–gel are described, including OIH classification, the interaction with the substrate, their advantages, and limitations. The main precursors used in the synthesis of OIH sol–gel coatings for corrosion protection are also discussed, according to the metallic substrate used. Finally, a multilayer system to improve the resistance to corrosion is proposed, based on OIH coatings produced by the sol–gel process, and the future research challenges are debated.

Keywords Coatings, Organic–inorganic hybrids, Corrosion, Sol–gel method

Abbreviations

AEA	Aliphatic epoxy acrylate
$Al(O^sBu)_3$	Aluminum tri-*sec*-butoxide
BTAH	1,2,3-Benzotriazole
BTMS	*n*-Butyltrimethoxysilane
CCCs	Chemical conversion coatings
DETA	Diethylenetriamine
DGEBA	Poly(bisphenol A-co-epichlorohydrin)
DMTMS	Dimethyltrimethoxysilane
ECO	Epoxidized castor oil
EGDMA	Ethyleneglycoldimethacrylate
ER	Epoxy resin
ERE	Epoxy-resin–ester
GMA	Glycidylmethacrylate
HDGS	Hot-dip galvanized steel
HEMA	2-Hydroxyethylmethacrylate
HMDIC	Hexamethylene diisocyanate
HMDS	Hexamethyldisilozane
HEPA	2,2′-Bis(4-β-hydroxy ethoxy) phenyl propane
HTMS	*n*-Hexyltrimethoxysilane
IBTMS	Isobutyltrimethoxysilane
IOTMS	Isooctyltrimethoxysilane
IPDIC	Isophorone diisocyanate
LDF	Linseed diol fattyamide
MAEP	2-Methacryloyloxyethylphosphate
MAPTES	3-Methacryloxy propyl triethoxysilane
MMA	Methylmethacrylate
n-PTMS	*n*-Propyl trimethoxysilane
OIH	Organic–inorganic hybrid
OTES	Octyltriethoxysilane
OTMS	Octyltrimethoxysilane
PAPTES	*N*-Phenyl-3-aminopropyltriethoxysilane
PDMSU	Bis[(ureapropyl)triethoxysilane] bis(propyl)-terminated-polydimethylsiloxane 1000
PDMMS	Polidymetilmetoxysilane
PFOTES	1*H*,1*H*,2*H*,2*H*-Per-fluorooctyltriethoxysilane
PR	Polyester resin
SiO_2-NP	Silica nanoparticles
SNAP	Self-assembled nanophase particle

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TBADP	Titanium(IV)-bis(acac)diisopropoxide
TDIC	Toluene diisocyanate
TEPA	Tetraethylenepentamine
TETA	Triethylenetetramine
TIBMS	Triisobutoxy(methyl)silane
TIPMS	Triisopropoxy(methyl)silane
TMCS	Trimethylchlorosilane
TMSPh	Tris-(trimethylsilyl)phosphate
ZrBTO	Zirconium(IV) butoxide

Introduction

Corrosion protection of metallic substrates using coatings is an active and important research area in materials science and in industry. Through the application of coatings, corrosion can be minimized and controlled by one of three main mechanisms (or by a combination of these), namely a barrier effect preventing the contact between the corrosive medium and the metallic substrate and preventing ion migration among the coatings; a cathodic protection where the coating material acts as a sacrificial anode; the use of inhibition/passivation species, including cases of anodic or/and cathodic protection, that inhibit the action of the external corrosive agents.

Technological development has led to the production of a large variety of coatings and materials that have an efficient barrier effect preventing corrosion, namely inorganic coatings, paints, and other surface treatments. Chromate and similar hexavalent chromium compounds are effective substances used as inhibitors and are usually incorporated in anticorrosive pretreatments of a wide range of metals and alloys. The high corrosion resistance offered by the use of chromate films is due to the presence of Cr^{6+} ions. One important example is chromate-based chemical conversion coatings (CCCs), as this surface treatment shows an enhanced corrosion resistance and improves coating adhesion. Nonetheless, the use of hazardous compounds, such as CCCs, volatile organic compounds (VOCs), and hazardous air pollutants (HAPs), has been restricted after studies about their impact on natural environments and human health showed them to be toxic and carcinogenic. As such, their application is heavily regulated by most environmental legislation.

The need for alternative environmental friendly materials and processes has been investigated, leading to an enormous effort in the search for novel materials. These materials must provide good corrosion protection performance as well the recommended environmental targets. During this period, researchers from civil and mechanical engineering, chemistry, materials, and corrosion sciences have tested a large variety of nontoxic and environmentally friendly processes and among them the sol–gel method has demonstrated to be an efficient alternative for the replacement of existing CCC technology.

Osborne[1] in 2001 reported the application of sol–gel methods for the production of gel coatings for metal corrosion protection purposes. The article entitled "Some observations on chromate conversion coatings from a sol–gel perspective" confirmed that new chromate-free materials obtained by sol–gel methods allowed flexible control of coating morphology and constituent oxide materials leading to enhanced properties of the conversion coatings. This report showed that the organic–inorganic hybrid (OIH) coatings produced exhibited promising properties of adhesion and corrosion protection. The obtained data also suggested that the OIH gel formulation might be tuned to contain nonsoluble chromium inhibitors regulating their effective concentrations within the coating layer.[1] The quick evolution of this specific research area and the potential contribution of sol–gel coatings as a corrosion inhibition system for metal substrates has led to several review publications.[2,3] As alternatives to the use of chromate for corrosion protection of aluminum aerospace alloys,[4] the use of sol–gel-derived coatings for improved corrosion resistance of aluminum and steel metal surfaces[5,6] and magnesium alloys[7] had also been debated.

OIHs obtained by sol–gel methods are a new generation of multifunctional materials with a broad spectrum of useful properties and a diversity of application potential. The name itself indicates the presence of both organic and inorganic components within the common matrix support. The inorganic part is formed from silicon or transition metal alkoxides via hydrolysis, while the organic part could be based on a diversity of molecules, and depending on how the matrix structure is produced, they can be segments of a quasi-continuous macromolecular domains grafting or bonding the inorganic skeleton. These two components (hydrophilic oxides and hydrophobic organic molecules) are normally difficult to combine within the composite network, and to achieve the interaction between them special reaction conditions must be applied.

The sol–gel OIH coatings are complex matrices where the intermolecular interactions between the macromolecular existing structures and metallic surface are extremely relevant to material properties, like low porosity and rigidity and adhesion to substrate. The conjugation of these interactions results in materials with enhanced protective properties against oxidation, corrosion, erosion, and good thermal and electrical insulation properties. Another technological advantage of these materials arises from their ability to be produced at room temperature conditions on an industrial scale using well established and low-cost methods like spray, dip and spin coating, flow coating, roll coating, doctor blading, and capillary coating processes or using any combination thereof.[8] Altogether, the reagents involved to produce such matrices have very low environmental impacts. The tested corrosion protection processes and materials based on sol–gel technology demonstrate positive performances when several properties are considered, such as corrosion resistance, adhesion, fatigue resistance, reliability, and quality control. Although some of the possible alternatives demonstrate promise for corrosion protection, continuous efforts are being made in improving the production of OIH materials with improved properties, the understanding of the mechanisms involved in coating production and consequently their corrosion protection performance.

OIH materials represent an important part of the R&D activities and technology portfolio in companies such as Bayer, Boeing GE, Honeywell, BASF, Akzo-Nobel, Sumitomo, ASAHI Kasei, ASAHI Glass, Dow Corning, etc. They are also important in more specialized enterprises (Henkel, Procter & Gamble, Wacker, Nissan Chemicals, Shin-Etsu, Toppan, Mitsubishi Chemicals, NEPES, Merck, MicroResistTechnologies, etc.). However, the present review is focused mainly on OIHs based on siloxane (i.e., at least one of the precursors used is a siloxane) gels produced by sol–gel-derived methods to improve resistance to oxidation/corrosion or to modify/activate the surface properties of metallic substrates, taken from studies at an academic level in the past few years (2001–2013).

Sol–gel process fundamentals and OIHs classification

The sol–gel process is a low temperature synthetic route and is generally used as a chemical route to synthesize OIH materials. It is particularly advantageous in the production of coatings as it provides an excellent control of precursor stoichiometry and as there are a large number of precursor reagents with tuned functional groups, a diversity of OIH gels could be produced following the same trends. This process also allows the incorporation of additional components that introduce complementary functions of the material such as UV protection, antifouling, antireflection, moisture resistance, corrosion inhibition, and adhesion protection. Moreover, the sol–gel process enables coating deposition on substrates with a large surface area involving simple and inexpensive equipment.

The definition of sol–gel method itself has undergone some changes over time. There are many authors with significantly different definitions, for example Dislich[9] considered that the sol–gel procedures are only those that take into account multicomponent oxides which are homogeneous at an atomic level. Under different circumstances, Segal[10] introduced the sol–gel method as the production of inorganic oxides in the form of colloidal dispersion or in the form of metal alkoxides. Others,[11] considered that the sol–gel process was any chemical process whose starting point was a solution resulting in a solid phase whether or not precipitate (even though the system did not result in a strong network). Given the diversity of definitions found, a broader sol–gel method definition was considered[12]: "every process that starts from precursor's solutions with intermediate stages including a gel and/or a sol." To begin the sol–gel process, the chemical compounds known as the *precursors* (Table 1), must be selected and dissolved in a certain liquid solvent (where necessary) where they will be chemically transformed, forming a *sol*. *Sols* are stable suspensions of colloidal particles within a liquid.[13,14] This first step is a typical chemical transformation aiming at the

Table 1: Chemical name, empirical formula, structure, and common abbreviation of some of the most commonly used precursors for the preparation of coatings by sol–gel method

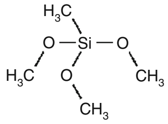
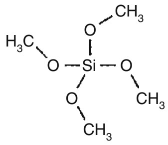
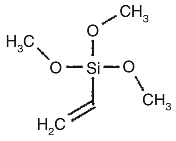
Chemical name	Empirical formula	Structure	Abbreviation
Methyltrimethoxysilane	$C_4H_{12}O_3Si$		MTMS
Tetramethylorthosilicate	$C_4H_{12}O_4Si$		TMOS
Vinyltrimethoxysilane	$C_5H_{12}O_3Si$		VTMS

Table 1: Continued

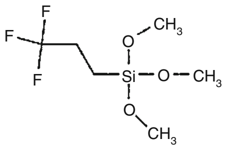
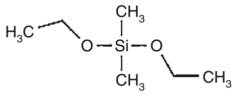
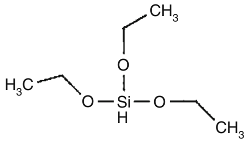
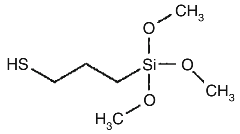
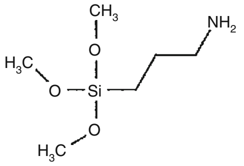
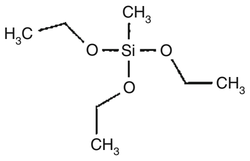
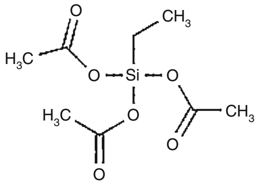
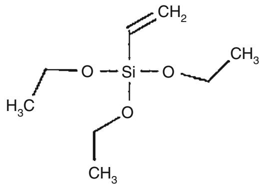
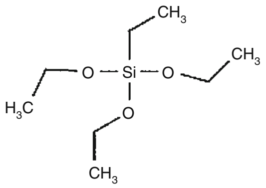
Chemical name	Empirical formula	Structure	Abbreviation
3,3,3-Trifluoropropyltrimethoxysilane	$C_6H_{13}F_3O_3Si$		TFPTMOS
Diethoxydimethylsilane	$C_6H_{16}O_2Si$		DEDMS
Triethoxysilane	$C_6H_{16}O_3Si$		TEOS
Γ-Mercaptopropyltrimethoxysilane	$C_6H_{16}O_3SSi$		MPTMS
3-Aminopropyltrimethoxysilane	$C_6H_{17}NO_3Si$		APTMS
Methyltriethoxysilane	$C_7H_{18}O_3Si$		MTES
Ethyltriacetoxysilane	$C_8H_{14}O_6Si$		ETAS
Vinyltriethoxysilane	$C_8H_{18}O_3Si$		VTES
Tetraethoxysilane	$C_8H_{20}O_4Si$		TEOS

Table 1: Continued

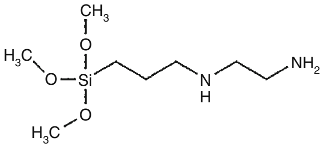
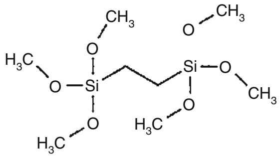
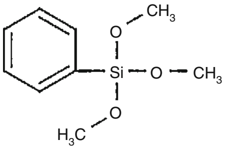
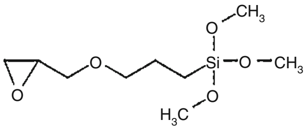
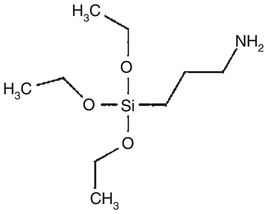
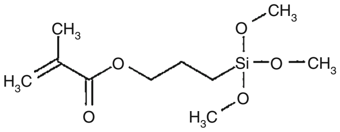
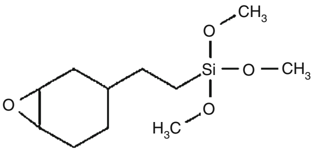
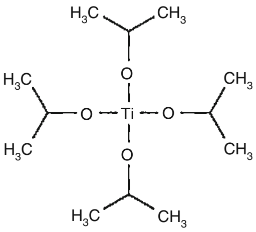
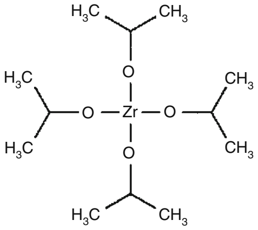
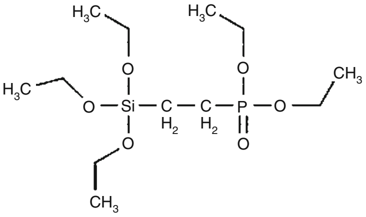
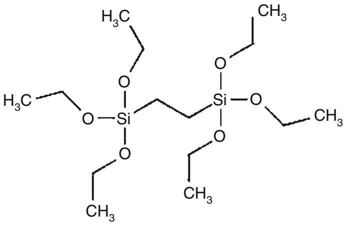
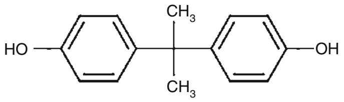
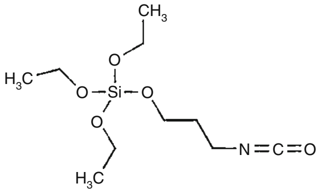
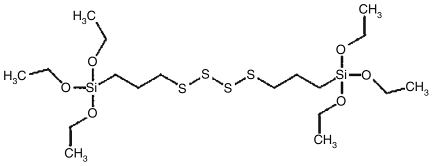
Chemical name	Empirical formula	Structure	Abbreviation
N-(2-Aminoethyl) 3-aminopropyl trimethoxysilane	$C_8H_{22}N_2O_3Si$		AEAPS
Bis(trimethoxysilyl)ethane	$C_8H_{22}O_6Si_2$		BTMSE
Phenyltrimethoxysilane	$C_9H_{14}O_3Si$		PTMS
3-Glycidoxypropyltrimethoxy-silane	$C_9H_{20}O_5Si$		GPTMS
3-Aminopropyltriethoxysilane	$C_9H_{23}NO_3Si$		APTES
Γ-Methacryloxypropyl-trimethoxysilane	$C_{10}H_{20}O_5Si$		MAPTS
2-(3,4-Epoxycyclohexyl)–ethyltrimethoxysilane	$C_{11}H_{22}O_4Si$		ECHETS
Titanium(IV) tetra-1-propoxide	$C_{12}H_{28}O_4Ti$		TIPT

Table 1: Continued

Chemical name	Empirical formula	Structure	Abbreviation
Zirconium(IV) tetra-1-propoxide	$C_{12}H_{28}O_4Zr$		ZrTPO
Diethylphosphonatoethyl-triethoxysilane	$C_{12}H_{29}O_6PSi$		PHS
Bis-1,2-[triethoxysilyl]-ethane	$C_{14}H_{34}O_6Si_2$		BTSE
2,2-Bis-(4-hydroxyphenyl)-propane	$C_{15}H_{16}O_2$		BPA
3-Isocyanatopropyltriethoxysilane			ICPTES
Bis-[3-(triethoxysilyl)-propyl]-tetrasulfide	$C_{18}H_{42}O_6S_4Si_2$		BTSTS

formation of a *sol* of colloidal particles or a solution of oligomers (small polymers). As *sol* is a fluid it can be cast in a mold, or be applied on the substrates using various shaping techniques[8] and can be stored for a certain time before further casting. After this process, a *gel* is formed and to achieve gelation, the chemical transformations in a *sol* must be allowed to proceed until a rigid and interconnected network forms, only limited by the walls of the container.[11] Another important step in the sol–gel art is the drying, which is a very critical one. When drying occurs under normal conditions, it usually results in a contraction of the gelled network. The resulting dry gel, commonly referred as *xerogel*, can be reduced in volume between five and ten times when compared with the initial wet gel.[11,13] This phenomenon involves the contraction deformation processes of the network and the transport of liquid through the pores of structure. If the gel is dried in wet supercritical conditions, the shrinkage will be minimal, and the resulting product is known as an *aerogel*. If the smallest dimension of the gel is more than a few millimeters, the material is classified as a *monolith* and when the gelation occurs by fast evaporation of the solvent, films and fibers will be produced (Fig. 1). However, owing to the loss of volatile by-products formed in the hydrolysis–condensation reactions, it is difficult to control sample shrinkage during three-dimensional network formation.[10,11,13,15–18]

According to Hench and West,[14] there are three approaches used to produce sol–gel *monoliths*:

Method 1: Gels obtained from gelation of colloidal solutions;
Method 2: Hydrolysis and polycondensation of alkoxide or nitrate precursors followed by hypercritical drying of gels;
Method 3: Hydrolysis and polycondensation of alkoxide precursors followed by aging and drying under ambient atmospheres.

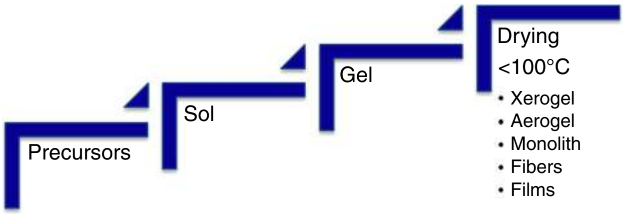


Fig. 1: Main steps to obtain materials by sol–gel processing (temperatures <100°C) (adapted from Hench and West[14])

Figure 2 shows the different routes of the sol–gel processing and their relation with the three systematic approaches proposed by Hench and West.[14]

The properties of an OIH gel material are not the simple addition of each individual contribution of its components. It depends on the chemical nature, on the size and morphology, as well as on the synergies established between each component. The diverse composition of these materials has led to specific classifications within OIHs. The influence of the interface is very important so its nature has been used to classify these materials.

In one of the earliest papers, published by Sanchez and Ribot,[19] OIH networks were divided into two general classes: class I and II.[19] Later, Wojcik and Klein[20] introduced a classification of three main classes based on OIH chemical structures. Class I includes the OIHs where the organic and inorganic components interact via hydrogen bonds, Van der Waals forces, or ionic bonds (Fig. 3).

Class II includes OIHs where the inorganic and organic components are connected by covalent bonds (as shown in Fig. 4). The support network is formed by condensation of chemical structural units (called gel precursors) where organic and inorganic components coexist. During the gel process, the addition of the precursor's structure replicates a stable macromolecu-

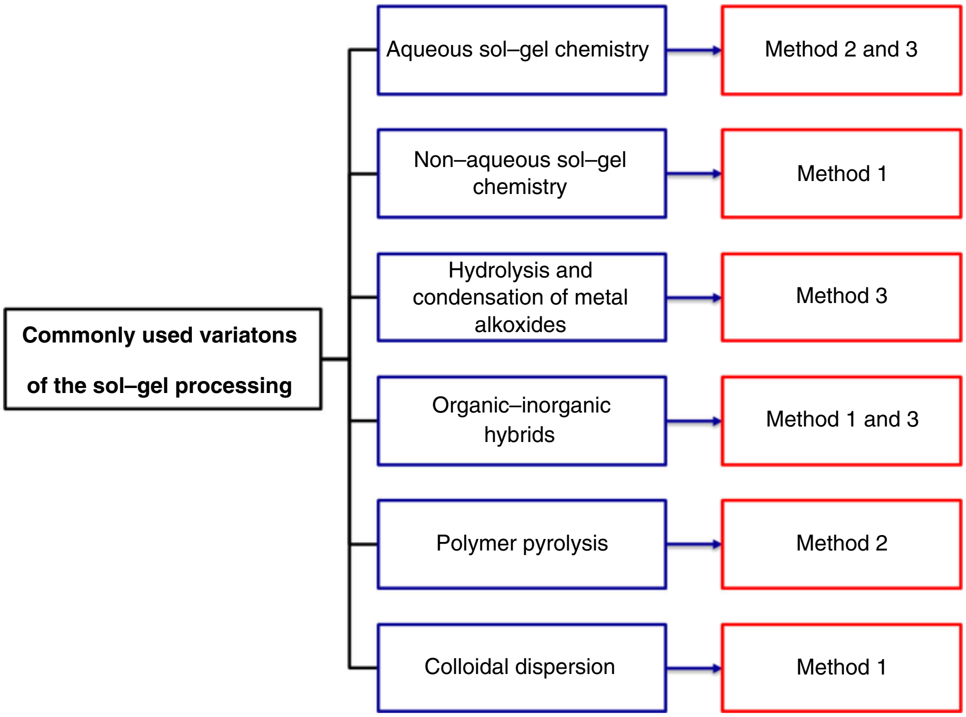


Fig. 2: Different routes of the sol–gel process and their relation with the three systematic approaches proposed by Hench and West[14]

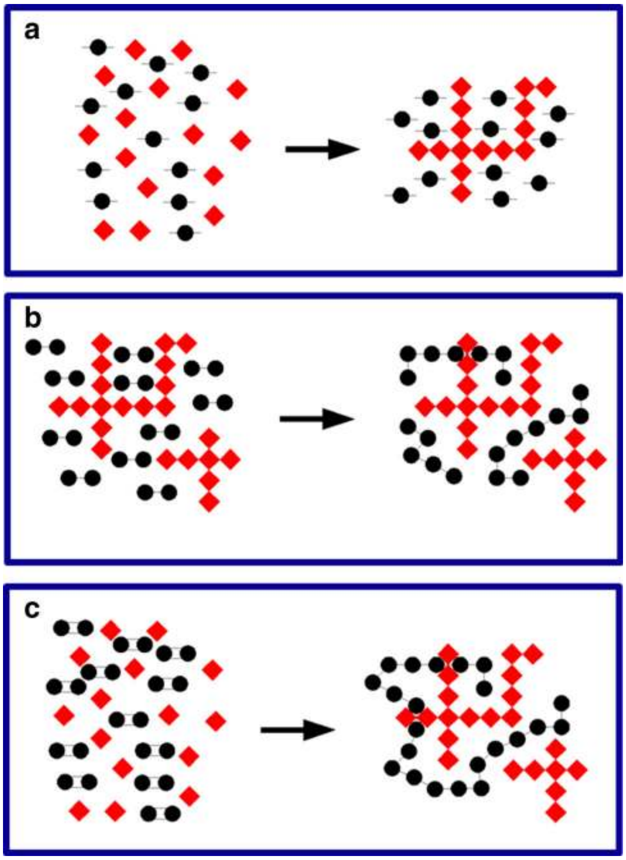
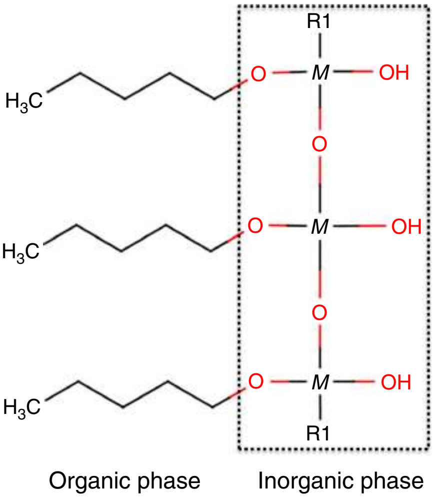


Fig. 3: Interactions established between the organic and inorganic components for OIHs class I. (a) ●- organic molecules immobilized in an inorganic network ◆◆; (b) ●● organic molecules embedded in an inorganic network ◆◆ followed by polymerization forming a semi-interpenetrating network; (c) simultaneous formation of two networks from organic molecules ●● and inorganic precursors ◆ forming an interpenetrating network (adapted from Prado et al.[21])



(M represents a network–forming element such as Si, Ti, Zr, Al, B, etc. R1 is typically an alkyl group)

Fig. 4: Organic–inorganic interactions for OIHs class II (adapted from Prado et al.[21])

lar network where these two basic components are chemically bonded.

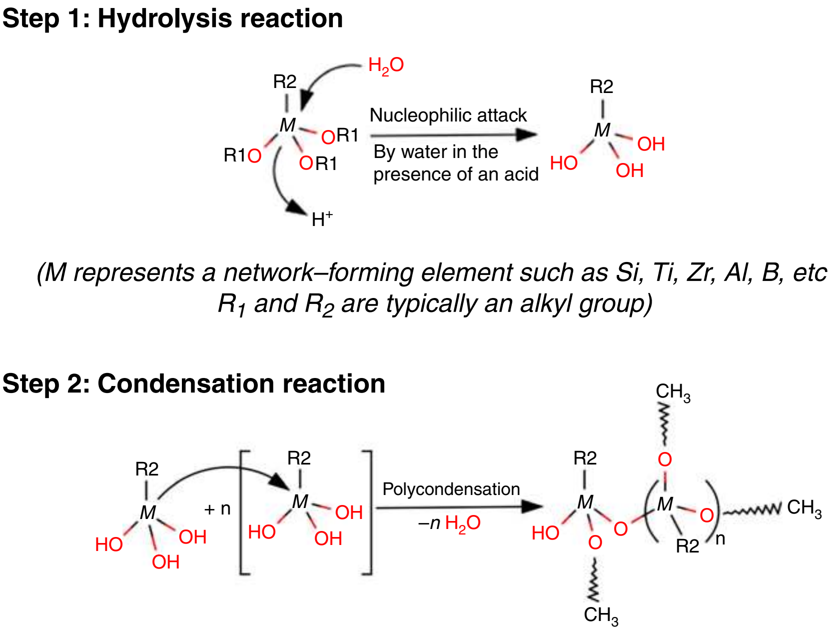
The sol–gel synthesis of OIHs class II based on siloxanes can be easily synthesized because Si–C$_{sp}$[3] bonds are rather covalent and therefore quite stable toward attack by nucleophilic species such as water, alcohols, and hydroxylated ligands, among others. The *precursors* of these compounds are organo-substituted silicic acid esters of general formula $R'_n Si(OR)_{4-n}$, bridged precursors of silesquioxanes $X_3Si–R'–SiX_3$ (X = Cl, Br, OR) in which R′ can be any organofunctional group and n is generally 1 or 2. Organic groups R′ may bind to an inorganic network with two distinct purposes, namely as *network modifiers* or as *network formers*. If R′ is a simple nonhydrolyzable group, it will have a network modifying effect. On the other hand, if R′ bears any reactive group that can, for instance, polymerize or co-polymerize (e.g., methacryloyl, epoxy, or styryl groups) or undergo hydrolysis-condensation (trialkoxysilyl groups), it will act as a *network former.*[16]

The synthesis of this class of OIHs usually involves polycondensation reactions between di-, tri-, or polyfunctional organosiloxanes and metal alkoxides (e.g., $Si(OR)_4$, $Ti(OR)_4$, $Zr(OR)_4$, etc.). Polyfunctional alkoxysilanes and metal alkoxides are effective crosslinkers allowing for the production of OIHs materials with mechanical and thermal properties between those of polymers and glasses. The results of hydrolysis and polycondensation of these precursors are organo-polysiloxanes that have properties such as hydrophobicity, corrosion protection, low dielectric constants, or good scratch resistance.[21] Due to the chemical and physical properties of the OIHs class II that are suitable to prevent corrosion/oxidation of the metallic substrates these are the main focus of this review.

The synthesis reaction involved usually results from the conjugation of two mechanisms, namely[12,13,16]: hydrolysis of metal alkoxides (step 1, Fig. 5) to produce hydroxyl groups in the presence of stoichiometric water (generally in the presence of acid or base catalyst) followed by polycondensation of the resulting hydroxyl groups and residual alkoxyl groups to form a three-dimensional network (step 2, Fig. 5).

The first step is the formation of a covalent bond between the organic and inorganic components giving rise to the "seed" precursor molecule. The conversion of the precursors into OIH materials proceeds via the formation of siloxane (Si–O–Si) bonds. This process takes place by hydrolyzing monomeric tetrafunctional alkoxide precursors employing a mineral acid (e.g., HCl) or base (e.g., NH_3) as a catalyst.

Figure 6 shows a schematic of a practical example including the generic steps in the preparation of a particular example of class II OIH material involving



(M represents a network–forming element such as Si, Ti, Zr, Al, B, etc. R_1 and R_2 are typically an alkyl group)

Fig. 5: Generic reactions involved in the preparation of OIH materials through sol–gel method (adapted from Brinker and Scherer[11])

the incorporation of a polyether oligomer within the gel matrix.[22]

Class III (Fig. 7) includes OIHs that are based on the combination of both types of interactions assigned to classes I and II. An example of this kind of hybrid is the material obtained by an organic polymer containing hydrolyzable alkoxylanes $(SiOR)_3$ and hydrogen acceptor groups such as carbonyls, amines, and imides.[21]

Sol–gel coatings for metals

Corrosion protection of metallic substrates has long been one of the key roles performed by organic coatings, one of the most cost-effective means of providing practical protection from corrosion to easily corrodible metallic structures and items. The production of eco-friendly sol–gel coatings to prevent corrosion on metallic substrates was one of the emerging areas of application, competing with conventional chromate and phosphate CCCs.

Corrosion protective coatings are not just a barrier layer between the object and its environment. They should act to: protect small and local areas of exposed substrate and stop the spread of damage; limit the passage of current on the substrate; slow/inhibit oxygen (and other oxidants') mobility toward the metal surface; minimize water and electrolyte penetration and release embedded inhibitor species that contribute to substrate passivation or block corrosion reactions.[23–28] Coating application or further removal processes should be performed with hazard-free procedures and environmentally friendly reagents as well as by producing eco-friendly residues.[29] The use of sol–gel method to produce coatings for corrosion protection fulfills the main requirements of what should be an environmentally friendly process. It is a waste-free method, excludes any washing stage, and is able to produce coatings with high specific pore volume, specific surface areas, and high purity. Due to low temperature synthesis (frequently close to room temperature), the thermal volatilization and degradation of entrapped species (such as organic inhibitors) is minimized. As liquid precursors are used in the synthesis, it is therefore possible to cast coatings in complex shapes and produce thin films without the need for machining or melting.

Processing of sol–gel-derived film coatings and their applications has been extensively reviewed before 2001[4,30] Metroke et al.[5] reviewed the recent advances in the use of sol–gel-derived coatings for improved corrosion resistance of aluminum and steel metal surfaces. Later, in 2005, the pioneering work of van Ooij et al.[6] demonstrated the applications of functionalized trialkoxysilanes to produce OIH gels, as a prospect for solving the problems of the metal finishing industry.[31] The traditional metal plating process in this industry involves, for instance, the use of CCC, lead, cadmium, and cyanide in plating baths. These authors have shown that distinct terminal organic groups of the functionalized siloxanes have a key role in the improvement of coating adhesion while the continuous inorganic network formed, largely silicate, provides the coating's mechanical strength and hydrophobicity,[6] minimizing/avoiding the hazards associated with tradi-

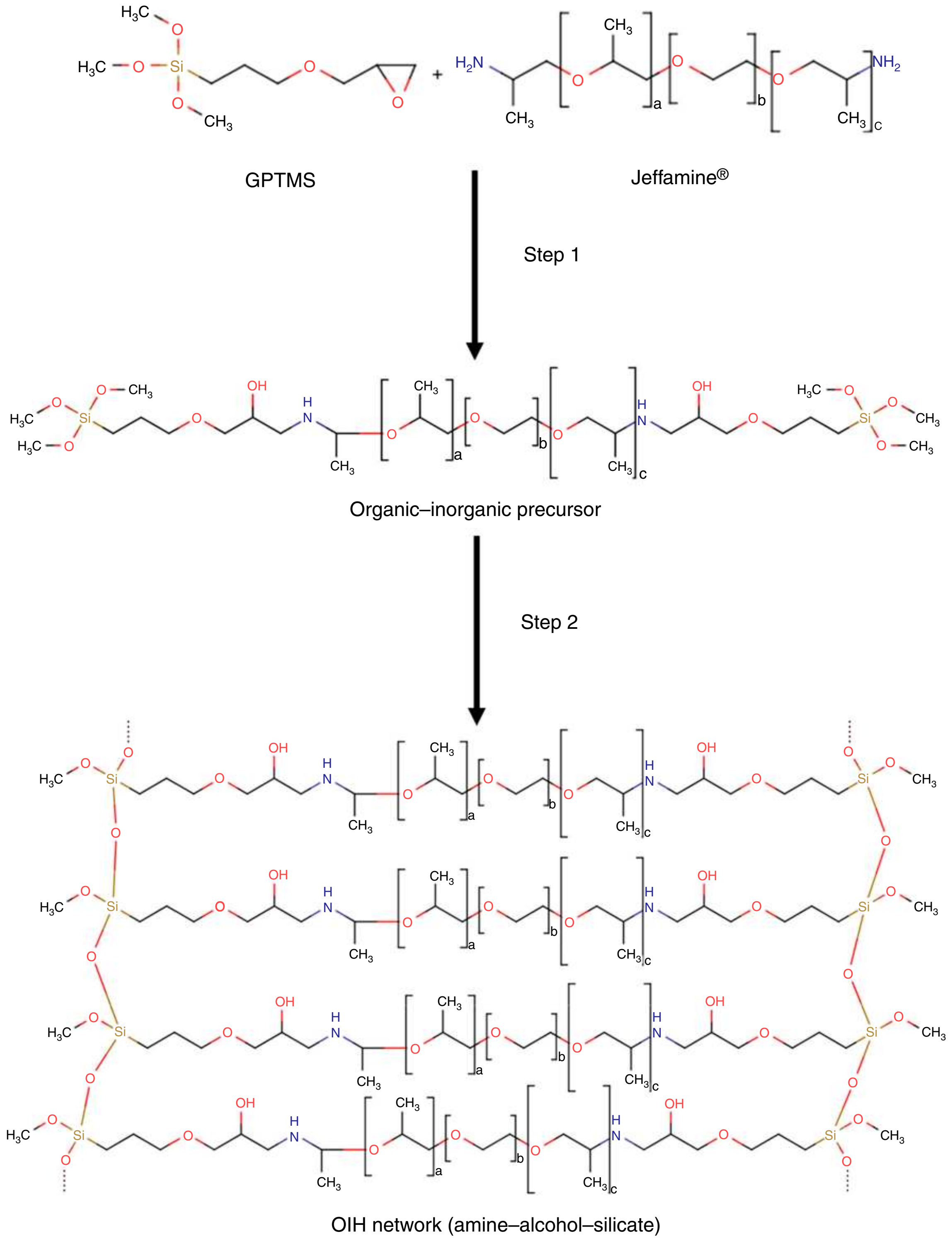
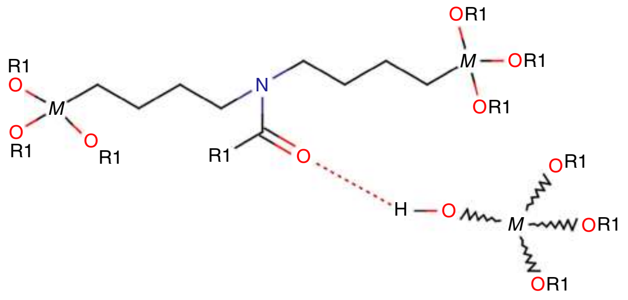


Fig. 6: Practical example of the generic steps involved in the preparation of OIH materials[22]

tional metal plating baths especially when it comes to heavy metals and cyanide.

In 2002, Gray and Luan[7] reviewed some the most relevant processes applied to the protection of magnesium alloys, namely electrochemical plating, conversion films, anodizing, gas-phase deposition, and laser surface alloying/cladding.[7] Since then, the research and progress on Mg alloys have improved rapidly across the world, as highlighted in the paper published by Wu and Zhang[32] where a detailed review is given about the state of the art methods of corrosion protection as well the patents regarding the



(M represents a network–forming element such as Si, Ti, Zr, Al, B, etc. R_1 is typically an alkyl group)

Fig. 7: Organic–inorganic interactions for OIHs class III (adapted from Prado et al.[21])

protection of magnesium alloys.[32] The authors found that although magnesium alloy-related patents exhibited a steady increase in the last 20 years, only a small amount was applied in industries.[10] In 2012, Hu et al. reviewed the progress in corrosion protection of magnesium alloys. The authors focused on the several types of existing coatings and on the techniques used to evaluate the corrosion performance of those coatings.[33]

Organic–inorganic hybrid (OIH) sol–gel coatings for corrosion protection

Organic–inorganic hybrid materials are the new generation of multifunctional materials with a broad spectrum of useful properties and diverse applications. The combination of inorganic with organic and/or bioactive components in a single material has led to many interdisciplinary scientific advances which can be seen in a large number of publications. Searches in *Science Direct*, *Springerlink*, *ECS Digital Library*, and *ACS Publications*, including the keywords “hybrid” and “sol–gel,” returned approximately 21,000 scientific articles that were published since 1990. A bar chart of the number of identified scientific publications (Fig. 8) shows that the number of publications in 2013 is about forty-five times the number of those published in 1990.

In the last few decades, the growing interest in developing new materials has led to the preparation of several organically modified silicates as potential metal corrosion coating materials.

Many material scientists and chemists, such as Schmidt[34] and Wilkes,[35] started to synthesize OIH materials by sol–gel processes and published a series of pioneering research articles. Since then, a diversified number of sol–gel-based protective coatings have been produced and tested. In the last few decades, the use of pretreatments based on siloxanes has been widespread due to their properties, namely the low cost and low environmental impact. Several studies have been carried out extensively since the early 1990s[6,8,36,37] and it has been demonstrated that siloxanes can be effective in protecting metallic substrates against corrosion (i.e., steel, aluminum alloys, zinc alloys, copper, and magnesium alloys). However, the need for tuned materials for specific purposes has led toward the production and development of new OIH gel materials which combine both the advantages of organic polymers (flexibility, lightweight, good impact resistance) and the features of inorganic material components (processability, high mechanical strength, excellent chemical resistance, and thermal stability).

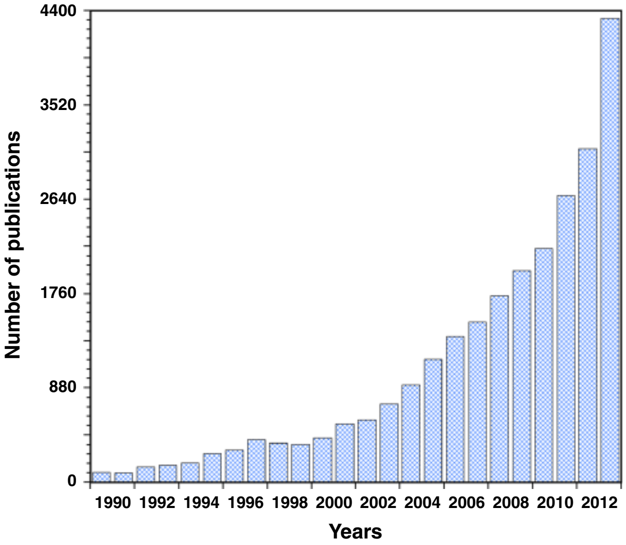


Fig. 8: Bar chart of scientific publications published from 1990 until 2013 found in Science Direct, Springerlink, ECS Digital Library, and ACS Publications using the key words “organic–inorganic hybrids”

Particular types of OIH materials have also been named, either as ORMOSILs (acronym generated from ORganically MOdified SILicates) or OMOCERs (from ORganically MOdified CERamics) depending on the precursors used (Table 1) and synthesis method.

The most effective approach in the production of OIH materials seems to be the sol–gel technique with its specific ability to create a spacious network (macromolecular network) containing M–O bonds under mild (room temperature) synthesis conditions either with or without a solvent.[21,38] Their properties are highly dependent on the degree of mutual phase dispersion (therefore dependent on the organic/inorganic ratio), the reactivity of crosslinking alkoxide reagents, the processing steps, and the solvents.[39] The presence of polymeric chains within the OIH matrix contributes to the material’s high electrical resistivity and impermeability, providing similar properties to the usual painting materials.

The hybrid structure maximizes the preparation of materials that could lead to efficient coatings against corrosion as well as ensuring primary technological needs.[40]

Over time, several review papers have been periodically published about OIH gels, giving an up-to-date description of state of the art contributions. The most important reviews published since 2000 are listed chronologically in Table 2.

Table 2: The main review articles about sol–gel processes since 2000

Year	Authors	Discussed subject matter
2000	Bescher and Mackenzie[41]	Review of the physical properties of sol–gel coatings
2002	Attia et al.[42]	Overview of sol–gel-derived coatings, namely the processes and optical applications
2007	Mackenzie and Bescher[43]	Usefulness of the sol–gel process in the synthesis of materials comprising nanoscale architectures. Description of the processing of semiconducting, metallic, ferroelectric, or scintillating nanoparticles in various oxide matrices
	Niederberger[44]	Review of nonaqueous sol–gel routes to produce metal oxide nanoparticles
2008	Sakka[45]	Review of the effects of the starting solution composition on the reaction in alkoxysilane solutions for the formation of bulk and fibrous materials, and the microstructure of a particular film coating
	Dimitriev et al.[46]	Summary of the most significant research achievements in sol–gel science and technology
2009	Kozhukharov[47]	Discussion of basic concepts related to sol–gel technologies, as well as the most important problems. Correlation of the properties of obtained products, synthesis conditions and the features of the methods applied
	Wang and Bierwagen[38]	Introduction of the basic chemistry involved in sol–gel processes, the progress and development of sol–gel protective coatings on metal substrates and alloys until 2007. Summary of the most relevant limitations of sol–gel coatings
	Benvenutti et al.[48]	Discussion of the properties and characteristics of hybrid materials related to experimental synthesis conditions
2011	Pandey and Mishra[49]	Description of synthesis routes to produce hybrid composite materials derived by combining the sol–gel approach and organic polymers
	Sanchez et al.[15]	Discussion of the major applications of OIH (biological based) materials
2012	Balgude and Sabnis[50]	Description of potential of sol–gel-derived hybrid coatings processes for the production of multifunctional pretreatments for metallic substrates
2013	Abdolah Zadeh et al.[51]	Discussion of the most relevant existing works on self-healing sol–gel coatings
	Chaturvedi and Dave[52]	Discussion of the methods to design nanomaterials where emphasis was given to the sol–gel method

In the nineties,[53] the OIH concept firmly emerged and an increased number of papers focusing on this area were published within a short period of time. In 2001, several important review papers on this subject were published. Schottner[54] and Walcarius[55] reviewed the perspectives of the hybrid sol–gel-derived polymers and reported the applications of OIH materials in the various fields of electrochemistry. Mitzi[56] selected examples of OIH films and discussed the techniques used on the deposition of OIH sol–gel materials.

Several authors focused review papers on aspects related with gel synthesis processes, like Hay and Raval[57] who reported on the use of the nonhydrolytic sol–gel route to synthesize OIHs. Arkhireeva et al.[58] synthesized in 2004 OIHs using both the hydrolytic and nonhydrolytic sol–gel routes. The authors showed that both routes produced OIHs. However, an improved control of the shape and particle size was obtained using the hydrolytic process. In the same year, Castelvetro et al.[40] reviewed and discussed the synthetic approaches to produce nanostructured OIH materials. The main focus was on processes and products that can be carried out in an aqueous medium, even though nonaqueous systems have also been discussed. Later in 2005, Sanchez et al.[59] summarized the general chemical pathways to prepare OIH materials and presented remarkable examples of applications of functional OIHs in several areas. The authors highlighted the use of protective coatings based on phenylsilsesquioxanes on structures for naval aircrafts and silsesquioxane–polyester mixtures in coil coating applications. The use of an OIH multilayer system on a mosaic panel of the 14th century "Last Judgment Mosaic" can be seen in the St. Vitus cathedral in Prague. The OIH multilayer system, highlighted by the authors, is composed by a functional layer of organo-alkoxysilanes and oxide nanoparticles, placed between the substrate and a fluoropolymer coating.[59]

The intense research efforts on this particular area have justified, almost yearly, a detailed review paper reporting state-of-art OIHs. The fundamental review papers were written by Innocenzi et al.,[60] Dash et al.,[61] Lebedev,[62] and Sanchez et al.[63]

Multilayer systems combining different sol–gel layers with different functions are also an area with high potential and have started to be exploited. The first detailed used of OIHs was a bilayer system to prevent corrosion of metallic substrates by the combination of a super-hydrophobic OIH coating and an OIH coating doped with corrosion inhibitors, proposed by Zheng and Li[64] in 2010.

OIH coatings for corrosion protection of iron-based alloys

Steel is the most common and versatile metal currently applied and can be classified either as carbon steel (CS) or steel alloy (SA). SA materials cover an extensive range of steels including low-SAs, stainless steel (SS), heat-resistant steels, and tool steels.[65] SS can be produced with a wide range of properties and can be used in many different industrial fields, owing to their mechanical and corrosion properties.[65] Steel surface substrates are traditionally passivated by the use of conversion coatings, phosphating, and chromating. These treatments produce a layer of corrosion products—the passivation layer—capable of resisting furthering chemical attack. However, due to the high toxicity associated with the use of chromates, several efforts are being made all over the world to find environmentally friendly treatments. OIHs obtained through sol–gel method are potential candidates as the presence of the metal oxides, on the treated steel surfaces, allows covalent bonding between the inorganic parts of the OIHs based on siloxanes (Si–O–metal oxide), as shown in Fig. 9, and making them suitable alternatives to the conventional conversion coatings.

The corrosion resistance behavior of sol–gel coatings or thin films deposited onto these particular metallic substrates has been extensively studied. The studies performed were mainly aimed at testing the capability of sol–gel coatings to improve oxidation and corrosion resistance of the substrate.

The most relevant information and conclusions gathered from the analyzed papers about the use of OIH gels based on siloxane (i.e., at least one of the precursors used is based on siloxanes) coatings are summarized in Table 3, which is organized according to date of publication. By analyzing the content of the collected bibliography, it was concluded that the study of alternative precursors for the production of new OIH materials, using sol–gel technology seems to have slightly evolved when compared with the amount of precursors available in the market.

Considering all the data gathered in Table 3 and Fig. 10, it is shown that only 13% of the OIH (class II) based on siloxanes were produced without the precursors TEOS, GPTMS, MAPTS, MTES, and MMA. It is also shown that TEOS is used in the majority of the publications found for these substrates. Although the number of publications has increased significantly over the past 4 years, the research for this type of substrates is still confined to a few precursors and this is especially notable when compared to studies published before 2008. This unusual behavior may be due to the search for the OIH coating with the optimum performance since the sol–gel method allows, with simple changes in the synthesis parameters, to obtain OIH materials with very distinct properties. The corrosion protection properties of OIH coatings are strongly dependent on their processing conditions, such as aging, reaction pH, curing temperature, and molar ratio of precursors. The statistic data referred to above suggests that the research efforts were more focused in optimizing the synthesis process instead of testing and studying new precursors.

The publications found focused mostly on the use of TEOS, GPTMS, MAPTS, and MTES including, in some cases, the performance of coating materials with embedded corrosion inhibitor species. Generally, the reported studies showed that those OIH coatings exhibit a promising performance in protecting the CS and iron-based alloys against corrosion. However, a comparative study between the properties of the OIH coatings obtained by each author was not possible since the methods and conditions used to evaluate the OIH coatings performance were not the same and the results themselves were not comparable.

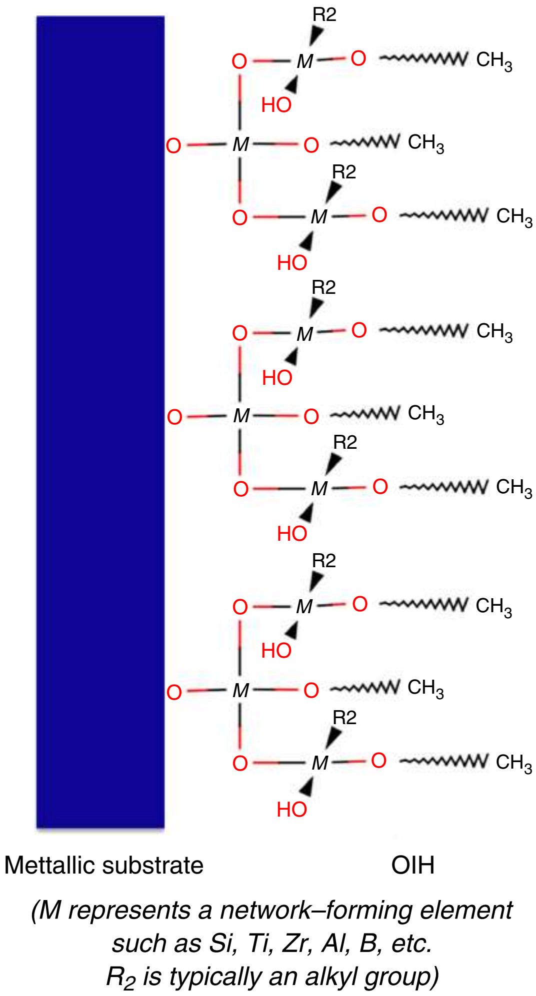


Fig. 9: Schematic representation of the interactions between OIHs class II and the metallic substrate (adapted from Prado et al.[21])

Table 3: Studies on corrosion protection using OIH (class II) sol–gel coatings on carbon, steel alloys, and SS substrates (2001–2013)

Year	Precursors	Results and conclusions	References
2001	TEOS, MAPTS	OIH coating enhanced corrosion protection, excellent film adhesion, and flexibility	66
2002	DGEBA, APTMS	OIH coatings studied offered corrosion protection	67
2003	TEOS, MAPTS	Uniform and defect-free coatings that enhanced corrosion protection	68
	GPTMS, AEAPS, APTES, MAPTS	Efficient coatings in protecting surfaces from external influences	69
2004	TEOS, MTES	OIH coatings showed high stability and resistance to pitting in simulated body fluids	70
	MTES, TIPMS, TIBMS	OIH coatings were thermally stable and the refractive index decreased with organic groups	71
2005	TEOS, MTES	Homogeneous and crack-free OIH coatings exhibited enhanced corrosion resistance	72
	TEOS, MTES	OIH coating adherence on the substrate surface was good and corrosion resistance of bare material improved	73
2006	GPTMS, TEOS	Passivation of the substrate was enhanced	74
	TEOS, MAPTS (SiO_2 gel/Dacromet)	Precursors produced a crack-free surface and enhanced the erosion–corrosion resistance of Dacromet	75
	TEOS, MTES	Crack-free and continuous coatings. Effective barrier against corrosive environments	76
2008	TEOS, MTES, GPTMS	OIH coatings exhibited good anticorrosion properties	77
	TEOS, MTES,$AlCl_3.6H_2O$,	Multilayer hydrophobic OIH coating with doped cerium nitrate provided good corrosion resistance	78
2009	TEOS, MTES	OIH coatings effectively protected the surface of the substrate against corrosion	79
	Silicone-epoxide resin (Silikopon EF)	OIH coating provided good corrosion resistance for substrates against alkaline, acidic, and saline conditions	80
	TEOS, MAPTS, MMA	OIH coating provided good corrosion resistance at OCP conditions	81
2010	TEOS, MAPTS	Best corrosion resistance for OIH coatings obtained with TEOS/MAPTS molar ratio = 2	82
	TEOS, MAPTS	OIH coatings increased the hydrophilic properties of the substrate surface and significantly improved the corrosion resistance in physiological media	83
	TEOS, MAPTS	OIH coatings with defect-free, smooth surface, and good substrate adhesion improved corrosion resistance	84
	TEOS, MAPTS, MMA	OIH film improved the barrier effect against corrosion	85
	GPTMS, ZrTPO	Coatings increased the corrosion resistance of substrate	86
	MAEP, MAPTS	Coating improved corrosion resistance when compared with the uncoated samples	87
2011	TIPT, PAPTES	Coatings were dense, uniform, defect-free and provide protection to the substrate against corrosion	88
2012	TEOS, VTES	OIH coatings showed to be a promising drug delivery system that can be applied to metallic implants	89
	TEOS, LDF	OIH produced showed a barrier action against different corrosive media	90
	TEOS, MTES	OIH films including 10 and 50 nm silica nanoparticles were produced and exhibited low corrosion current density	91
	GPTMS, TIPT	Silane-titania hybrid coating with inhibitor-loaded nanocontainers showed the best performance	92
	TEOS, MAPTS, MMA	OIH coatings prepared protected the substrate against corrosion	93
	GPTMS, $Al(O^sBu)_3$	Influence of cerium concentration on behavior against corrosion of the OIH coating was studied	94
	TEOS, MAPTES	Barrier properties of the OIH coating were improved by the incorporation of inorganic fillers	95
	TEOS, MAPTS, MMA	Anticorrosion properties of the OIH improved when the MAPTS was added to the formulations	96

Table 3: Continued

Year	Precursors	Results and conclusions	References
	n-PTMS, TEOS	Both pure OIH and copper oxide-OIH coatings improved the corrosion resistance of the substrate	97
	TEOS, MTES, PTMS	OIH coatings derived from methyl-substituted organically modified silane exhibited superior barrier properties	98
	GPTMS, BPA	Cerium-doped OIH coatings protected the substrate effectively	99
	TEOS, ZrTPO	Corrosion behavior of the substrate was enhanced	100
2013	TEOS, MAPTS	Addition of polyethyleneglycol within the OIH allowed improving the barrier effect and the corrosion behavior of the coating	101
	TEOS, MAPTS, MMA	Smooth, crack-free, adherent OIH coatings containing carbon nanotubes protected the substrate against corrosion	102
	GPTMS, $Al(O^sBu)_3$	Correlation of the influence of temperature on the chemical and structural transformation of the xerogel with the mechanical properties	103
	GPTMS, MTMS	OIH coatings had excellent substrate adhesion and improved corrosion behavior	104
	GPTMS, OTES, ZrBTO	OIH coatings were produced and prevented the oxidation of the substrate	105
	TEOS, MPTMS	OIH coating synthesized with $Ce(NO_3)_3$ as catalyst showed improved corrosion behavior of the substrate	106
	GPTMS, TEOS	Thermally cured cashew nut shell liquid-based OIH coatings were developed and increased corrosion resistance properties	107
	GPTMS, TEOS	Corrosion resistance of the OIH films was improved when a phosphoric acid pretreatment was done	108
	TEOS, MTES	OIH coatings enhanced the corrosion resistance of samples	109
	ER, APTES	OIH coatings studied showed good corrosion resistance performance in neutral and acidic environments	110

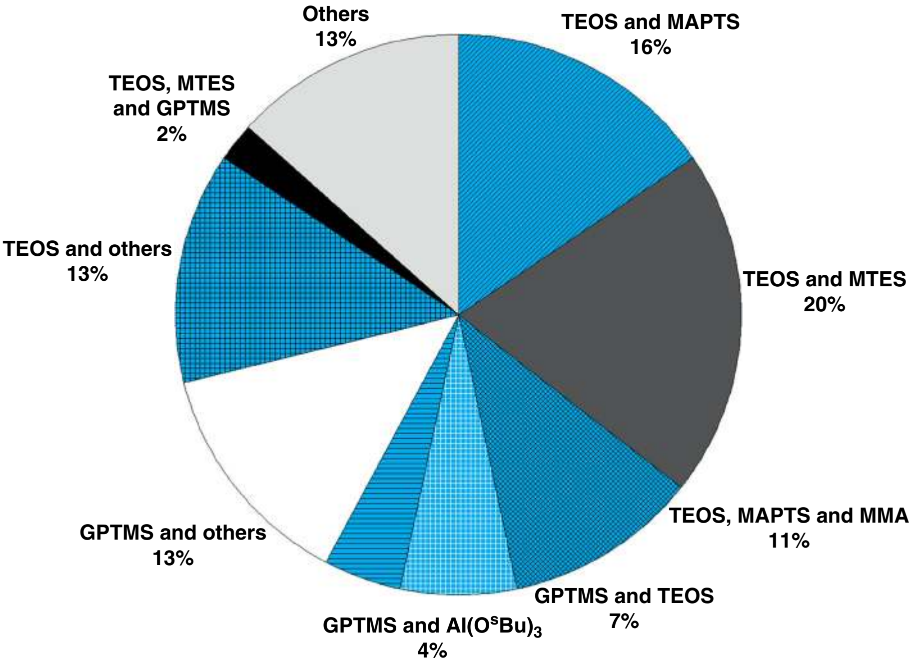


Fig. 10: Distribution of publications according to the type of precursors used for the production of OIH (class II) gel coatings based on siloxanes (i.e., at least one of the precursors used is based on siloxanes) for carbon steel and iron-based alloys (2001–2013)

The extensive use of TEOS may be due to the fact that this precursor was studied in detail and its properties and reactivity are quite well known at different pH and temperatures.[11,111] Furthermore, it is less toxic when compared to TMOS,[112] it is available with a higher purity grade at a relatively low price and has a relatively slow and controllable rate of reaction.[49] OIHs based on TEOS can produce, at low temperatures, homogeneous films on large areas of substrates[113] and its addition improves the transparency of the OIH materials.[112,114] Moreover, OIHs based on TEOS are low cost as this reagent is about four times cheaper than GPTMS and half of the price of MTES, for similar purity grades.

OIH coatings for corrosion protection of aluminum-based alloys

Aluminum-based alloys are a group of materials with a wide range of applications due to their physical and processability properties, namely low density, easy shaping (in rolling, drawing and extrusion), high corrosion resistance in different environments, easy machining, colorless and nontoxic corrosion products, and high thermal and electrical conductivity together with low aluminum cost, less than 2000 USD/ton. Those characteristics make aluminum-based alloys of remarkable economical and industrial importance.[38,65]

Examples of applications using aluminum-based alloys include building structures, panels, machined components, electro–mechanical components, vehicles and accessories, tools, machine making, shipbuilding, packing, architecture, etc. Aluminum alloys are chosen in these applications due to their natural tendency to form a passivation Al_2O_3 layer, which can also be artificially generated by anodizing the substrate. Nevertheless, this passivation layer deteriorates when in contact with aggressive media, such as those containing chloride ions (particularly seaside environments) resulting in pitting corrosion.[38] To overcome this drawback CCC treatments are usually used due to their effectiveness in corrosion protection of these alloys. However, as stated before, conversion layers based on Cr(VI) should be avoided and substituted with coatings environmentally friendly. OIH class II sol–gel coatings are potential candidates because, in addition to the OIHs coating properties, these materials can provide a stable Si–O–Al (Fig. 9) bonding between the inorganic functionality of these materials and the formed passivation layer (Al_2O_3).[115]

Table 4 gathers the information collected from the published papers where OIH class II sol–gel coatings

Table 4: Studies on corrosion protection using OIH (class II) sol–gel coatings on aluminum-based alloys substrates (2001–2013)

Year	Precursors	Results and conclusions	References
2001	GPTMS, TEOS	Comparative studies showed that OIH film provided better corrosion protection than the CCCs	116
	GPTMS, TMOS	Incorporation of cerium into sols appears promising for protection against substrate corrosion	117
2002	GPTMS, TEOS	Curing agents were studied. The amine curing agent produced films with good corrosion resistance	118
	GPTMS, TMOS	Nature of the curing agent significantly influences film structure and the corrosion resistance properties of the OIH film (curing agents studied: CF_3SO_3H, HPF_6, DETA, TETA, TEPA)	119
2003	GPTMS, TMOS	Thin and dense protective surface OIH coatings doped with corrosion inhibitors improved corrosion protection	120
	GPTMS, TEOS, MTES	Addition of particles to OIH coatings notably improved the final corrosion protection properties	121
	GPTMS, AEAPS, APTES, MAPTS	OIH polymers were efficient in protecting surfaces from external influences	69
	GPTMS, TMOS	Investigation and characterization of the SNAP coating process	122
2004	TEOS, VTMS, MAPTS, MTMS, DMTMS, *n*-PTMS, BTMS, IBTMS, HTMS, IOTMS, OTMS	Modification of produced thin OIH films with various concentrations of alkyl-modified silanes was found to enhance the corrosion resistance properties of the films on substrates. Hexyl-modified silanes exhibited the highest pore resistance and contact angle values	123
	TEOS, VTMS, MAPTS	Corrosion resistance characteristics depended on the nature and concentration of diluent used. The choice of solvent enables tailoring of the OIH coating structure	124
	MTES, TIPMS, TIBMS	Films were thermally stable, remaining without cracks on the substrates after heat treatment at 800°C	71

Table 4: Continued

Year	Precursors	Results and conclusions	References
2005	GPTMS, TMOS, BPA	OIH coatings were uniform, defect-free, relatively dense, presenting good adhesion and improved corrosion protection	125
	GPTMS, BPA	Coatings obtained improved corrosion protection by forming an impenetrable barrier to water and corrosive agents	126
	GPTMS, TMOS	Superior adhesion and corrosion protection make SNAP surface modification a promising alternative	127
	GPTMS, TEOS, VTMS, MAPTS	OIH coatings efficiently inhibited the corrosion of the substrate	128
	GPTMS, TMOS	Inclusion of corrosion inhibitors within the coating has a pronounced effect on reducing a corrosion attack on the substrate	129
	GPTMS, TEOS, ZrTPO	OIH coatings with incorporated zirconium oxide nanoparticles doped with a cerium inhibitor provided long-term corrosion protection	130
	GPTMS, ZrTPO	OIH sol–gel systems showed potential for aerospace uses in comparison with conventional CCCs	131
2006	GPTMS, TEOS, ZrTPO	OIH coatings provided corrosion protection and may be used as an alternative for pretreatment of the substrate	132
	GPTMS, TMOS	Formation of resilient films with good barrier properties	133
	GPTMS, TEOS	OIH prevented the corrosion of the substrate	134
	HEPA, ICPTES, MAPTMS, AEA	UV-curable OIHs were synthesized and characterized with good adhesion to the substrate	135
	GPTMS, TEOS	Film provided an impenetrable barrier to water and corrosive agents	136
2007	TEOS, MAPTS	Transparent coatings obtained by UV curing adhered well and were robust in scratch and abrasion tests	137
	GPTMS, TEOS	OIH coatings showed good corrosion resistance in contact with an NaCl solution	138
	GPTMS, TEOS	OIH films provided an effective barrier to water and corrosive agents with a good corrosion resistance	139
	GPTMS, MTMS	OIH coatings were uniform, continuous, crack-free and acted as an efficient barrier against corrosive electrolytes	140
2008	TFPTMOS, TMOS	OIH film prevented infiltration of H_2O and limited the exposure of corrosive elements to the substrate	141
	GPTMS, TEOS	Incorporation of different inhibitors into the silane solution enhanced protection effectiveness of the OIH film	142
	GPTMS, TEOS, APTMS	OIH coatings with good thermal stability and excellent corrosion protection under open-circuit conditions	143
	GPTMS, ZrTPO, TIPT, TBADP	OIH films showed good anticorrosive performance and excellent adhesion	144
	GPTMS, ZrTPO	Studies about the impact on the barrier properties of the OIH sol–gel coatings due to the addition of corrosion inhibitors	145
	PDMSU	PDMSU/PrOH coatings showed improved corrosion behavior when compared to PDMSU/EtOH coatings	147
	TEOS, MAPTS, SiO_2	OIH sol–gel coatings promoted substrate corrosion protection and the presence of inhibitors was studied	146
	GPTMS, TMOS	Creation of a dense crosslinked OIH coating improved substrate corrosion protection	147
	GPTMS, MTMS	Uniform and crack-free coating was obtained reducing corrosion current	148
	MAPTS, TEOS	TEOS addition into the coating enhanced the electrochemical corrosion resistance	149
2009	TEOS, MAPTS, EGDMA, SiO_2.	Multilayer coatings enhanced the corrosion resistance	150
	GPTMS, MTMS, PR	Corrosion current of the coated substrates decreased when compared to the bare substrate	151
	TEOS, MPS, HEMA	Electrochemical measurements displayed better barrier properties than the uncoated substrate	152
	GPTMS, TEOS	OIH films created provided excellent barrier and corrosion protection compared to bare substrate	153

Table 4: Continued

Year	Precursors	Results and conclusions	References
	GPTMS, TEOS, MTES, BPA, SiO_2-NP	OIH gel coatings with uniform thicknesses and nanoparticle distribution reduced the corrosion rate	154
	TEOS, MPTMS, PTMS	Addition of inhibitors to OIH coatings led to an improvement of active corrosion protection	155
	BTMSE, MPTMS	OIH coatings improved the corrosion protection of metals	156
	TEOS, APTMS, IPDIC, HMDIC, TDIC	OIH gel coatings showed improved corrosion resistance compared to commercial nonchromate pretreatments	157
2010	TEOS, MAPTS, SiO_2, EGDMA, GMA	Multilayer systems exhibited limited barrier properties due to the porous structure of the sol–gel film	158
	GPTMS, ZrTPO	Hydrotalcite addition to sol–gel films improves the corrosion resistance of the coated substrate	115
	GPTMS, ZrTPO	Metallic surface treatment influences the corrosion resistance of the coated substrate	159
	MAPTS, ZrTPO	Zirconium nanoparticles significantly improved the performance of the OIH coatings	160
	GPTMS, TMOS	Cerium nitrate was excellent for self-healing of the OIH coating, while cerium chloride had no obvious effect	161
	GPTMS, TMOS	OIH coating showed good corrosion resistance	162
	TEOS, APTES, ECO	Corrosion tests showed excellent performance providing protection to the substrate	163
	GPTMS, ZrTPO	Crack-free sol–gel coatings with improved corrosion protection were produced on the alloy surface	164
	APTMS, IOTMS, ICPTES PFOTES	OIH coatings exhibited good corrosion inhibition	167
	(SiloXel) silane-I, silane-II, silane-III, TiPT	SiloXel acted as an invulnerable barrier against corrosion of the substrate	165
	BTSTS	Substrate covered by film and by silane conversion coatings showed better corrosion performance	166
2011	GPTMS, ZrTPO	Addition of as-synthesized hydrotalcite to the OIH film increased the barrier properties	167
	GPTMS, TEOS, BPA, APTES, MTES, SiO_2	Increasing the doping level of inhibitors did not lead to improvement of the corrosion resistance	168
	GPTMS, TMOS	Corrosion protection of substrates by aromatic diamine crosslinked OIH sol coatings was demonstrated	169
	GPTMS, TEOS	Coatings exhibited a good anticorrosion performance	170
	MAPTS, $Nb(OCH_2CH_3)_5$	Inclusion of niobium into the matrix significantly improved the coating corrosion protection properties	171
2012	GPTMS, $Al(O^sBu)_3$	Study of the inhibitor concentration influence on anticorrosion and mechanical properties of the OIH coating	172
	GPTMS, TMOS	Studies on synthesis and structure of an OIH coating deposited on the substrate	173
	GPTMS, TEOS, BPA, APTES, MTES, SiO_2	OIH coatings doped with cerium and transition metals showed promising corrosion protection properties	174
	GPTMS, TEOS, MTES, BPA	OIH coating without additives provided a good corrosion protection of the substrate	175
	GPTMS, ZrTPO	Zeolite microparticles used as reservoirs for Ce(III) were introduced into OIH coatings enhancing the corrosion protection of the substrate compared to the blank OIH coating	176,177
	GPTMS, ZrTPO	OIH coating corrosion properties were improved when red mud particles added were previously calcined	178
	GPTMS, MTMS	OIH coatings showed to improve corrosion protection of the substrate	179
	TEOS, MTES	OIH films doped with 1 mol% of lanthanum oxide induced a delay on the corrosion of the substrate	180
	GPTMS, DETA, ER	Coatings doped with inhibitor provided long-term corrosion protection of the substrate	181

Table 4: Continued

Year	Precursors	Results and conclusions	References
2013	GPTMS, TEOS	OIH coatings with good mechanical and adhesive properties were produced by optimization of the process parameters	182
	TEOS, MTMS	Investigation of dopants within the OIH system on the bond strength of the coating and the substrate	183
	GPTMS, ZrTPO	OIH coating containing cerium molybdate nanowires improved the corrosion protection of the substrate	184
	GPTMS, TEOS	OIH coatings showed good corrosion barrier properties and the doped ones revealed self-healing behavior	185
	GPTMS, MTMS	OIH showed good adhesion to the substrate and "appreciable" corrosion resistance	186
	GPTMS, TEOS, MTES	Corrosion protection of the OIH coatings doped with sodium montmorillonite and Ce(III) was improved	187
	GPTMS, TEOS	Pretreatment with the OIH delays the access of aggressive species to the barrier layer	188
	GPTMS, TEOS	OIH coatings protected the substrate against corrosion	189
	MTES, SiO_2	OIH showed good adhesion to the substrate, smooth, crack-free, and good corrosion resistance	190
	GPTMS, TEOS	Proper choice of parameters led to OIHs that protect the substrate against corrosion	191
	TEOS, APTES, ECO, TIPT	OIH films showed good adhesion to the substrate and good corrosion protection	192

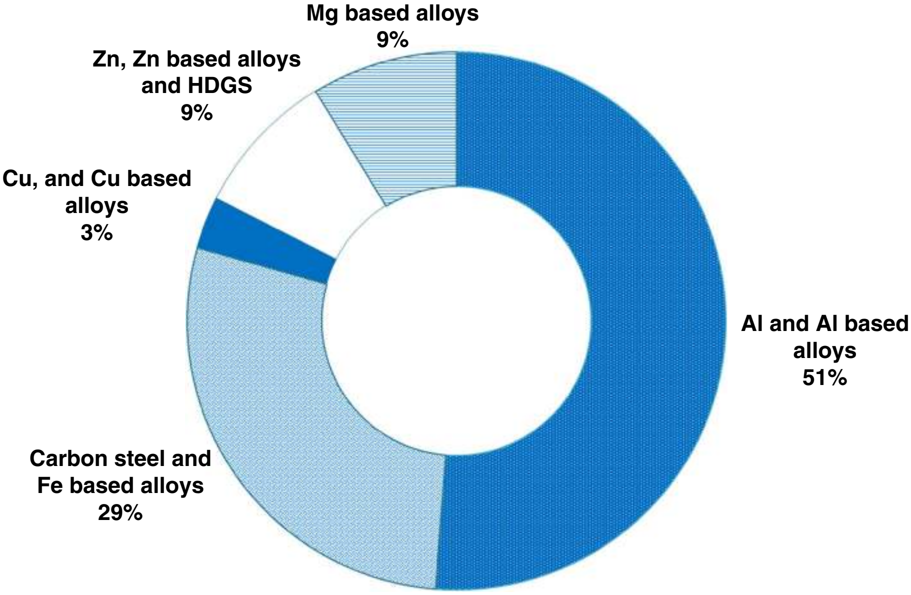


Fig. 11: Reported substrates coated with OIH (class II) gel coatings based on siloxanes (i.e., at least one of the precursors used is based on siloxanes) (2001–2013)

based on siloxanes (i.e., at least one of the precursors used is based on siloxanes) have been produced and tested on aluminum-based alloys. As shown (Table 4), research efforts in coating development for this specific set of materials are particularly strong and are not only focused on corrosion protection but also on aspects such as changing surface hydrophobicity/hydrophobility. For aluminum-based alloys, more precursors were tested than for CS and steel-based alloys substrates (Table 4). Considering the information gathered, half of the published papers were applied to aluminum-based alloys (Fig. 11). It should also be noted that the extensive research in seeking protective coatings for aluminum-based alloys against corrosion has been extensively championed by the aviation industry since it is the most commonly used material.

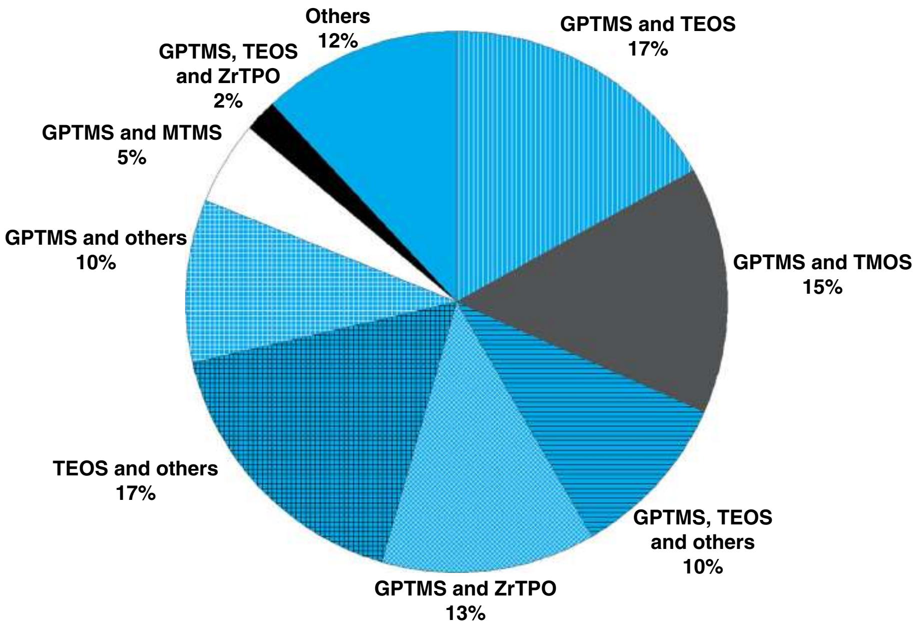


Fig. 12: Precursors used for the production of OIH (class II) gel coatings based on siloxanes (i.e., at least one of the precursors used is based on siloxanes) for aluminum-based alloys (2001–2013)

Considering all the information gathered in Table 4, Fig. 12 shows that 12% of the OIHs (class II) based on siloxanes reported were produced without using TEOS, GPTMS, TMOS, ZrTPO, and MTMS precursors. It is also shown that TEOS is present in 46% and GPTMS in 72% of the publications found for aluminum-based alloys. The collected data also shows that the research focuses mostly on the use of TEOS, GPTMS, TMOS, and ZrTPO and includes, in some cases, the performance of coating materials with embedded corrosion inhibitor species and the deposition of multilayers produced by several deposition-curing cycles.

The intensive use of TEOS is explained by the reasons stated in the previous section, with a lower price than MTMS or ZrTPO, boosting the search for effective OIH coatings using this specific precursor.

The use of GPTMS reported in 72% of the publications found for these substrates may be explained by the fact that this precursor is a combination of two different components, in particular, *glycidoxy* (organic) and silicon *alkoxy* (inorganic) groups. It can thereby form, at the same time, an organic network through the polymerization of *glycidoxy* groups and an inorganic network through the hydrolysis and subsequent condensation reactions of *alkoxy* groups.[134] Moreover, it can be used as a binder in organic–inorganic silica-based systems increasing the density and improving adhesion to the substrates.[125] It should also be mentioned that this precursor has an *epoxy* terminal group that exists as a component of commercially available epoxy glues that have an intensive industrial and domestic use for a large variety of purposes and application.

The most recent publications (since 2007) also showed that the innovations for coatings on these substrates are moving toward self-healing coatings doped with nanocontainers able to release entrapped corrosion inhibitors.[193–195] The majority of the OIH coatings studied showed promising performance in protecting the aluminum-based alloys against corrosion. Some of the OIH coatings studied have reached a remarkable degree of development and the next step will undoubtedly be large-scale industrial production and marketing.

OIH coatings for corrosion protection of copper-based alloys

Copper and copper-based alloys are versatile materials. This group of alloys has a wide application in sculptures, kitchen utensils, heat exchange tubes, tube sheeting, valves, and piping in seawater and fresh water systems.[65] Copper shows excellent corrosion resistance and scaling, high mechanical strength, high temperature resistance, and lifetime resistance to UV degradation. However, in wet environments its corrosion processes are accelerated. OIH sol–gel coatings have also been investigated for the protection of copper and the few studies found are summarized in Table 5.

Figure 12 shows that only 3% of the considered papers report tests using OIH class II based on siloxanes (i.e., at least one of the precursors used is based on siloxanes) and Table 5 shows that the most used precursor was GPTMS.

The reduced number of publications could be explained by several reasons. The native copper oxide

Table 5: Studies on corrosion protection using OIH (class II) sol–gel coatings on copper and copper alloys substrates (2001–2013)

Year	Precursors	Results and conclusions	References
2003	GPTMS, MTMS, SiO_2	OIH coatings show good resistance to UV and effectively delayed corrosion on the substrates	41
2008	GPTMS, MPTMS	Incorporation of 5 mol% of MPTMS enhanced the corrosion resistance	196
2009	BTMSE, MPTMS	OIH coatings have improved the corrosion protection of the substrate	156
2013	TEOS, GPTMS	Best corrosion protection was achieved when the amount of BTAH equals the molar number of epoxy group in the OIH coating	197
	TEOS, TMCS, HMDS	OIH coatings prepared in alkaline conditions are more stable and those prepared with HMDS were not affected by corrosion	198

layer is mechanically weak and at room temperature consists mainly of Cu_2O or both Cu_2O and CuO with a thickness of a few nanometers and is usually contaminated by carbon.[199–201] Additionally, the oxide layer is not easily wettable by the sol solution,[200] therefore the adherence between OIH sol–gel coatings and the substrate is compromised. Deflorian et al.[202] showed in 2008 that GPTMS does not establish an interaction with the native copper oxide layer. Moreover, 1,2,3-benzotriazole (BTAH, $C_6H_5N_3$) is an effective corrosion inhibitor for copper and its alloys in different environmental media, as demonstrated by Finšgar and Milošev[203] in a paper published in 2010, where the most significant work made using BTAH was reviewed. Therefore, it is neither a huge concern nor an urgent need to search for alternatives against corrosion for these types of substrates and alloys as BTAH shows to be a very effective corrosion inhibitor.

OIH coatings for corrosion protection for zinc-based alloys HDGS

Zinc is used as an additive in certain rubbers and paints, in the production of alloys, and as coating through several methods, such as electroplating, thermal spraying, sherardizing, hot dipping, etc.

Hot-dip galvanizing (HDG) is considered the most important zinc coating process to protect building structures, such as roofs and exterior walls, and constituent parts of cars and boats. Due to its superior corrosion protection by serving simultaneously as a sacrificial anode and as a physical barrier, zinc coatings are widely used. However, during contact (such as storage and transportation) with humid environments, the zinc surfaces form corrosion products (white rust, Fig. 13) easily due to the high electrochemical reactivity.

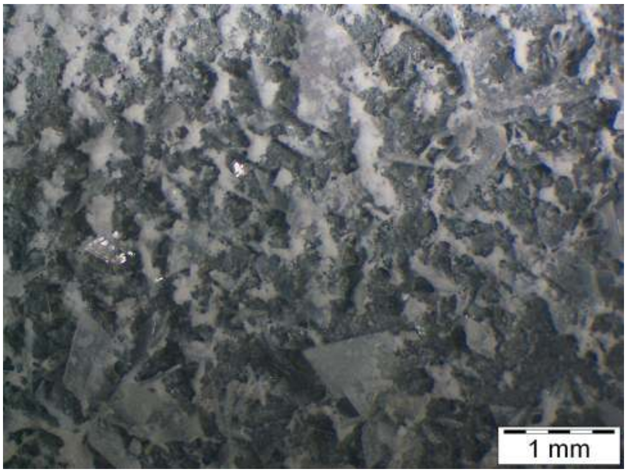


Fig. 13: Stereomicroscopic observation of HDGS surface magnified 20 times showing the corrosion products (white rust)

Hot-dip-galvanized steel (HDGS) used in reinforced concrete structures is an example of the many applications of HDGS and has been recognized as an effective measure to improve the service life of reinforced concrete structures. Although, when HDGS is embedded in fresh concrete, which is a highly alkaline environment, the zinc coating corrodes until passivation occurs and the concrete hardens. Due to the initial high corrosion rate of the zinc when in contact with fresh concrete, part of the zinc layer may be removed, compromising the galvanic protection of the underlying steel in the long term. Moreover, the hydrogen evolution during the corresponding cathodic half-cell reaction will increase the porosity of the adjacent cement paste and, therefore, reduce the bond strength between the rebar and the concrete. To minimize the zinc corrosion, either during storage and transportation within humid environments or when embedded in fresh concrete, CCCs have been extensively used. Nevertheless, these should be replaced in the near future due to their high toxicity. Several studies have been made to search for viable alternatives to the use of the CCC. However, few papers have been found using OIH sol–gel technology and these are listed in Table 6.

Considering all the information gathered (Table 6; Fig. 10), it was shown that only 9% of the papers

Table 6: Studies on corrosion protection using OIH (class II) sol–gel coatings on zinc, zinc-based alloys, and HDGS substrates (2001–2013)

Year	Precursors	Results and conclusions	References
2001	ER and BPA	Results showed effective protection of the metallic substrate	204
2004	MAPTS, TMOS	Anticorrosive performance of the Ce^{3+} ions trapped within the OIH network occurred by the self-repairing mechanism of the inhibitor	205
2006	TEOS and PDMMS	OIH coating improved corrosion protection of the substrate	206
	TEOS and MTES	Protective properties of OIH coating and its dependence on the sintering temperature were studied and shorter sintering times are recommended	207
2009	GPTMS, TEOS, MTES	Results showed that the OIH ensured a barrier effect against water and oxygen and acted as an adhesion promoter between the substrate and the coating	208
2010	GPTMS, TEOS, MTES	OIH filled with montmorillonite nanoparticles and cerium oxides enriched montmorillonite nanoparticles were tested. Cerium oxides did not improve the corrosion protection of the OIH film	209
	GPTMS, TEOS, MTES	Effect of the EPD conditions on HDGS pretreated with OIH was studied	210
2011	TIPT, PAPTES	Results showed that the OIH coating offered good corrosion protection for the substrate	88
2012	GPTMS, TEOS, MTES	Montmorillonite clay was modified to obtain Ce(III) montmorillonite clay and it was successfully incorporated in the OIH coating	211
	AEAPS, epoxy resin	OIH coatings with nanocontainers loaded with corrosion inhibitor enhanced the anticorrosive properties compared to the coatings with empty nanocontainers or only with the inhibitor	212
2013	GPTMS, TEOS, MTES	The beneficial effect of Na-Montmorillonite sonication on the corrosion properties of the OIH was confirmed	104
	GPTMS, BPA	OIH coatings doped with 0.05 M of cerium nitrate improved barrier properties	213
	BTSE, ERE	Substrates coated with OIH by EPD showed improved corrosion protection than the substrates coated with OIH by immersion	214
	ICPTES, Jeffamine®	OIH coatings minimized the H_2 evolution on the HDGS when embedded in fresh mortar	215

published between 2001 and 2013 tested OIH (class II) gel coatings. The most frequently used precursors were GPTMS, TEOS, and MTES and their use represented 36% of the total studies found and reported (Table 6). The small amount of published papers using OIH sol–gel coatings based on siloxanes (i.e., at least one of the precursors used is based on siloxanes) may be due to the focus on searching for new green conversion coatings[216–221] based on molybdate,[216–218] permanganate,[219,220] silicate,[222–224] titanate,[225,226] rare earth salts,[227–230] tungstate,[230,232] and vanadate[233] compounds.

OIH coatings for corrosion protection of magnesium-based alloys

Magnesium is employed as a structural load bearing material exploiting its chemical and metallurgical properties. These alloys are used as a sacrificial anode to protect steel against corrosion in circumstances such as the protection of underground pipelines and to increase the service life of household hot water tanks. In 2010, Guo[2] stated that due to the low weight and excellent mechanical properties of magnesium and its alloys, innovative magnesium alloys, or enhanced alloys with superior properties should be developed and in-depth research should be performed. Several alloys have been developed in order to obtain a range of properties and features that can fulfill the needs of a wide range of uses.[2,65]

The wide range of potential applications of magnesium and magnesium-based alloys makes it incredibly attractive for engineering uses, mainly in the aerospace and automobile industries due to the low density and high specific stiffness. Currently, magnesium-based alloys are under study and alloys referred to as AZ91D, AM60B, AM50A, and AS41B have been developed for die casting processing giving rise to alloys with superior corrosion resistance when compared to the aluminum die casting alloys frequently used. In spite of these advantages their application is still limited by their high corrosion vulnerability in aqueous environments, particularly in the presence of chloride ions.[65]

The publications found about the use of OIH (class II) coatings based on siloxanes (i.e., at least one of the precursors used is based on siloxanes) are summarized in Table 7. Considering all the information gathered, Fig. 10 shows that 9% of the papers were about

Table 7: Studies on corrosion protection using OIH (class II) sol–gel coatings on magnesium substrates published since 2001

Year	Precursors	Results and conclusions	References
2005	MAPTS, MPTMS, SiO_2	OIH coatings provided corrosion protection by sealing pores in the anodized layer and acting as a barrier. The application of multilayers eliminated the diffusion paths for corrosive species	234
2006	TEOS, PHS	Besides the barrier coating on a metal surface, the phosphonate functionalities reacted with the surface of the substrate increasing both adhesive and corrosion resistance properties of the coatings	235
2008	GPTMS, ZrTPO, TBADP	A well-adhered OIH gel coating for the substrate was obtained and the effectiveness of corrosion protection was confirmed	236
2009	TEOS, MTES, DEDMS, PHS, GPTMS	Corrosion protection was improved by implementing an interpenetrating network coating morphology	237
	TEOS, GPTMS	Study of the OIH coating properties, characterization and formation mechanism	238
	GPTMS, TMOS	Phosphate conversion coating sealed with OIH coating doped with inhibitor (2-methylpiperidine) showed better corrosion resistance than undoped coating	239
	TEOS, GPTMS	Three layers of OIH coatings totally covered the cracks produced on the molybdate conversion coating first deposited on the substrate and showing good corrosion behavior	240
2010	ZrTPO, GPTMS	OIH gel coatings doped with corrosion inhibitor showed improved corrosion behavior in the protection of the films in comparison with the undoped ones	241
	TMOS, DEDMS	OIH coatings obtained were evaluated as autonomous protective coatings as well as a pretreatment prior to acrylic topcoat. OIH coatings doped with Ce^{3+} were effective as pretreatments for a final acrylic coating	242
	GPTMS, VTES	Increasing of $[Ce^{3+}]$ on the OIH coating decreases the anticorrosion effect	243
2011	TEOS and MTES	Precursor ratios (X1), sol dilution (X2), and sintering temperature (X3) were studied for an OIH coating. Best conditions obtained for X1 = 3.36, X2 = 1.5, and X3 = 222°C	244
2012	GPTMS, MTES	Results revealed that the surface conditioning process was a key step to achieve the required anticorrosion properties of the substrate coated with the OIH	245
2013	GPTMS, $Al(O^sBu)_3$	OIH coating showed lower thickness in some points offering inferior protection against corrosive species	246
	DGEBA, APTES, APTMS, GPTMS, TMSPh	OIH coatings proposed showed high corrosion resistance with considerable improvements obtained by the OIHs based on APTMS and APTES	247

magnesium-based alloys and that in 71% of those publications the most frequently used precursor was GPTMS in combination with others.

Analyzing the available research papers concerning the prevention of corrosion on magnesium alloys, it seems that the research is following another path.[248–254] Most research focuses on improving the existing magnesium alloy properties[249–251] or inventing new ones,[248,252–254] instead of investigating OIH sol–gel coatings. This line of thought explains the fewer publications found when compared with the research available for aluminum or steel substrates.

Limitations of organic–inorganic hybrid sol–gel coatings for corrosion protection

In the last two decades, the existing knowledge about sol–gel processing and relations between structure and properties has had an exceptional development. Consequently, the research efforts on this particular area of materials science have grown, allowing scientists to gain knowledge on how to develop new OIH gel materials.

Despite the advantages of combining different properties, synthesis constraints still 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 thermal treatments (curing/drying) are crucial factors to ensure the quality of anticorrosive coatings.[3] Cracks may affect several properties and are detrimental to the substrate in wet corrosive media. Sendova et al.[255] produced silicate sol–gel coating films with four different crack patterns, achieving reproducible patterns by controlling the film deposition parameters. These authors showed that the geometric characteristics of the crack patterns were related to the thickness of the film and the deposition parameters. Latella et al.[256] synthesized and assessed the adhesion behavior and mechanical properties of OIH coatings. It was confirmed that the presence of a thermally grown oxide layer on the substrate, prior to the OIH sol–gel deposition, had an important role on the adhesion behavior (quality) between the film and the substrate. They also showed that the relation between the structure of the film and the mechanical properties of the coatings were influenced by the nature/characteristics of the organic substituent.

Mammeri et al.[39] investigated and analyzed the mechanical properties of OIH gels reported by several authors and concluded that those properties were dependent on their micro- and nanostructures as well as the nature and extent of the organic–inorganic interfaces within the gel matrix.

Some authors showed that when the substrate was subjected to localized plastic deformation due to impact with objects, or extensive plastic deformation due to substrate bending, cracks, and delamination developed easily in the thin films.[3,55] Others showed that electrodeposition (EPD) techniques provided fairly thick crack-free sol–gel-derived coatings when compared either to dip or spin coating techniques.[64,195] Castro et al.[257] combined the sol–gel method and the EPD process to prepare thick coatings onto metallic substrates obtaining crack-free deposits up to 20 μm in thickness after drying and crack-free glass-like coatings of 12 μm in thickness after sintering at 500°C for 30 min.[257] The characterization of OIH materials by potentiodynamic methods showed that they have good performance against corrosion. Most of the studies reported in the literature were on planar samples and the films were deposited by dip or spin coating processes. Objects with complex shapes are far more challenging to coat using these methods, particularly if a uniform thickness is a strict requirement. For these reasons, additional coating methods besides spraying, dipping, spinning, and EPD are expected to be extensively tested and developed in the near future.[3]

The deposition method selected might be a limiting variable as in certain circumstances it could negatively influence the performance of the OIH coating applied on the substrate. If the deposition method chosen is not the correct one, even with an OIH material displaying excellent barrier properties, the coating performance is compromised. The available deposition methods do not ensure fully uniform coatings, particularly when dip-coating systems for the deposition of low viscosity OIH gel precursors are used. Representative SEM images and EDS analysis data obtained for the HDGS samples coated with two matrices of the OIHs synthesized and deposited on the substrate by dip-coating method as described elsewhere[215] are shown in Figs. 14 and 15.

It can be observed that the distribution of the OIH coatings is not uniform. As shown by EDS analysis, the gray areas correspond to the OIH coating (assigned by high peaks of C, Si, and O) and the lighter areas are representative of the substrate (HDGS). In the absence of the OIH coating, the peak assigned to zinc is particularly intense. It is also highlighted that it is difficult to achieve a uniform distribution even with a triple-dip step process as shown in Fig. 15a. Nevertheless, these obstacles can be overcome by the use of intermediate deposition and curing steps. However, the increase in the number of steps involved in coating methods make these procedures extremely complex and time consuming. As such, a compromise between the improvement of the final material properties and the associated costs should be made.

Another important limitation considered by the consumer industry is the difficulty in assessing the behavior of the coating against corrosion after being exposed to the environment. In certain cases, such as underground pipelines and storage tanks, visual observation is impossible without exceptional efforts and

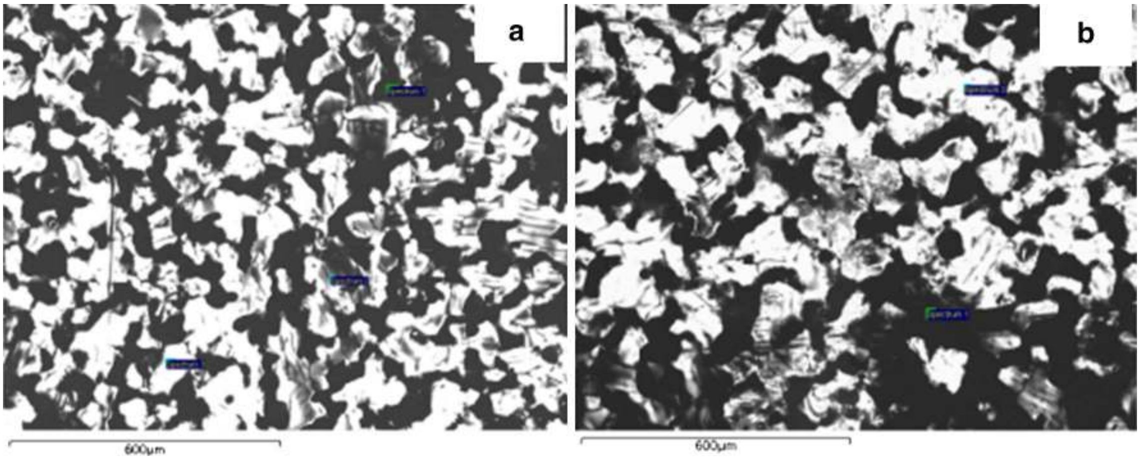


Fig. 14: SEM images of HDGS samples coated with the same OIH matrix by dip step method (a) one layer and (b) two layers

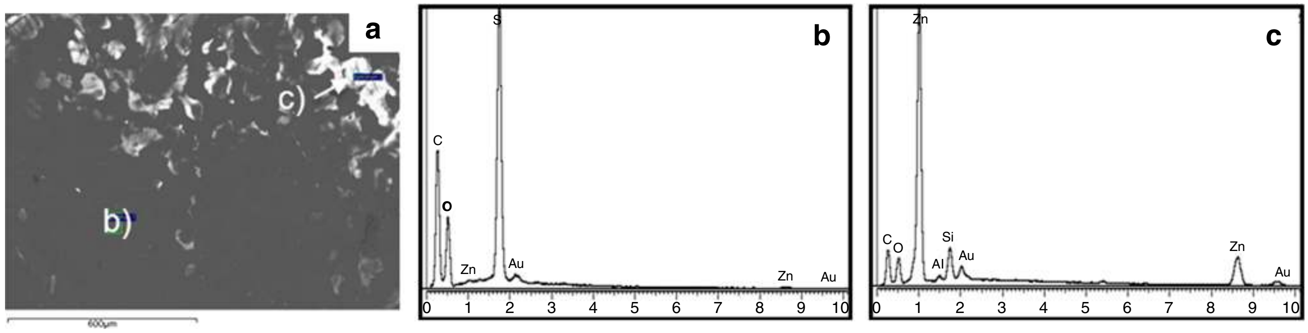


Fig. 15: (a) SEM image of HDGS samples coated with three layers of OIH by dip-coating method; (b) and (c) show EDS spectra obtained by scanning two different regions coated samples with three layers of OIH using dip-coating method

costs. In such situations, research should be carried out by pre-evaluating the performance and lifetime of the protective coatings, on lab or at a pilot scale, to plan the adequate maintenance/replacement interventions or by the development of appropriate sensors and monitoring methods based on self-sustainable and remote control devices.

Arkles[258] in 2001 published a paper about the commercial applications of the synthesized OIH gel materials and, according to him, these show viability in the market either owing to uncommon properties that allow new end-use applications or significantly better cost/performance relation when compared with the available materials.

Until now, the traditional CCCs confer the best corrosion protection known at controlled costs making this area even more challenging leading to continuous research for contemporary OIH materials that fulfill the same properties and performances exhibited by CCCs coatings.

It is noteworthy that no report has yet been found, either in industrial or academic research, of OIH sol–gel coatings with the same production costs and of equal or superior corrosion performance to traditional conversion layers used processes (chromating and phosphating). As far as authors are aware, no systematic theoretical and experimental approach on how to evaluate the viability, efficiency, and stability of OIH sol–gel coatings, has been implemented and is far from being established. The present situation demands further research and innovation efforts to guarantee the success of the application of OIH sol–gel coatings as metal corrosion protection.

Future and research challenges on organic–inorganic hybrid materials for corrosion protection

Nowadays, metal corrosion protection is strongly reliant on organic and organic–inorganic coating technology, as it is a cost-effective mean of providing practical protection against corrosion for easily corrodible metallic structures and objects. The quality and effectiveness of corrosion control by coatings is assumed by many users to be low cost and easy to achieve. For these reasons, the users of corrosion control coatings often choose these by cost and appearance and not by cost effectiveness, which can be measured by their performance and the lifetime of their behavior. However, with high labor costs and the difficulties found in recoating large, buried, complex or difficult to reach objects, more coatings users are focusing on the total costs of corrosion prevention and control. A coating system that increases the lifetime of the product but is somewhat more expensive, due to the initial application method, will pay for itself in reduced maintenance costs and reduced need for expensive recoating. Following this line of thought, the cost analysis of the corrosion protection provided by coatings must lead to further research into measuring and predicting the pot life of the protective properties of these materials.

It is undeniable that future applications and research should be focused primarily on the investigation of more environmentally friendly precursors and industrial colloid particles to replace the traditional precursors in the formation of sol–gel protective coatings without changing their general properties. Among the most critical constraints identified are the coating's mechanic strength and good adhesion to metallic substrates.

In spite of the large number of papers published on this subject, no work was found reporting the use of OIH coatings to stop and prevent corrosion on already damaged substrates as well as studies testing such materials for significant periods of time. The evaluation of whether OIH coatings have the ability to minimize/stop damage caused by corrosion and their durability over time is of extreme importance since OIHs are known for having a limited shelf life due to sluggish condensation reaction kinetics. The products developed for the protection of metallic substrates against corrosion must have a long lifetime. Another conclusion of the detailed analysis of the large set of publications was that studies on the barrier properties of the coatings over time were not found. Therefore, a relevant question that must be answered is ‘‘How long are OIH coatings used to prevent corrosion able to maintain their barrier properties?’’ As such, it is vital to undertake long-term tests in the near future as the durability/resistance of OIH coatings for corrosion prevention remains unknown.

The search for future OIH gel-based coatings is oriented toward low cost, pollution-free, easily synthesized, and effective corrosion protection OIH coatings that do not generate hazardous waste during their application and removal. Development of OIH coatings with self-healing properties would be a challenging innovation that will contribute in giving an added high-value to the synthesized materials.

Inspired by living organisms, materials engineers are focusing on developing materials with self-healing properties. According to Ghosh, the term ‘‘self-healing’’ may be defined as ‘‘…the ability of a material to heal (recover/repair) damages automatically and autonomously, that is, without any external intervention.’’[259] Several authors[195,260–272] developed and reviewed corrosion protection systems with self-healing abilities. The development of OIH coatings with those properties by incorporating the release of healing agents, reverting crosslinks or using simultaneous technologies such as conductivity; shape memory effect; nanoparticle migration; and co-deposition[257] might be considered as important achievements.

The development of new OIH coatings with dual-behavior (a protective barrier accumulating the OIH properties with a self-healing response) is a synergy that will bring benefits and improvements in corrosion prevention, fulfilling the requests needed by the users of coatings technology. This new concept is based on multilayer coatings where inhibitors and self-healing agents are immobilized in one of the layers being isolated from the external media and metal substrate by intermediate layers.[273] It is important that the implemented procedure to obtain these new systems assures good adhesion and similar thermal expansion coefficients between the layers. This same procedure also relies on an efficient top coating layer barrier protection. Moreover, the immobilization of both self-healing and inhibitor agents within a layer apart from the metallic substrate, by intermediate layers, prevent side reactions and leakage that may affect the substrate.

Considering the potentialities of the sol–gel method, efficient multilayer coatings could be produced if the adhesion between the metallic substrate and the contact layer is achieved, as well as the adhesion between each one of the different upper layers. Additionally, these materials show efficient barrier properties and the capacity of hosting species with different properties allows the development of an improved multilayer coating that combines corrosion inhibition and self-healing properties.

This paper proposes a model inspired by the one proposed by the authors Hughes et al.[273] for a multilayer coating system. The protective coating proposed is to be produced in five steps (Fig. 16), using mainly sol–gel methods. The first step involves chemical activation of the metallic surface, aiming to improve further covalent interaction between the Si–O–Si groups of the OIH matrix and the oxo- and/or hidroxo-groups formed on the metallic surface. Additionally, it is expected that this treatment will contribute to improving the uniformity and distribution of the first OIH sol–gel layer deposited, providing full coverage on a smoother substrate than that given by the chemical pretreatment. The second step of the proposed model consists of depositing a thin layer of OIH matrix gel. The sol–gel precursors used to produce this coating material should provide good adhesion with the activated metallic substrate and adequate curing process ensuring appropriate mechanical and support properties to the deposition of a second OIH gel layer. The composition of this and the other layers should be based on the same matrix composition in order to avoid sharp differences of the properties at the interface between the different layers preventing surface/interface tensions. This strategy also contributes to minimizing the differences in thermal and mechanical properties between the different layers. The deposition of this first layer is also necessary to ensure that the inhibitors and any other species, including self-healing agents, do not migrate toward the metallic surface except when in the presence of external aggressive agents. In this situation, the inhibitor action could be expanded to the vicinity of the metallic surface to stop the spread of corrosion.

As observed by several authors, the relative amount of inhibitor could compromise OIH matrix stability,[94,99,117,120,130] so the presence of the first OIH layer also contributes to additionally enhance the protection against inhibitor mobility/migration or diffusion toward the metallic surface.

The layer where the inhibitor is immobilized is produced in a third step and under adequate gelling conditions to minimize the curing demanding time and optimize the immobilization of the inhibitor species within this layer. Adjusting the gelling time (viscosity) of the gel precursor (of the deposited coating) by achieving an optimum viscosity value, allows the starting of the curing process immediately and during a short time. This methodology should also obtain a dense and smooth layer with a good adhesion to the previous OIH layer.

The following step consists of producing a third OIH layer containing self-healing agents that contribute to guarantee the reversibility of the damages caused by a variety of factors such as usage, weathering, or loading damage. The reversibility mechanism could be triggered by the entrance of water and ions transported through the topcoat. This mechanism is inspired by the process that has been used for self-healing in polymer composites through the release of a polymerizable healing agent that can bridge cracks after reaction with the appropriate catalysts.[274] The synthesis procedure to obtain this layer is critical as it should ensure that the

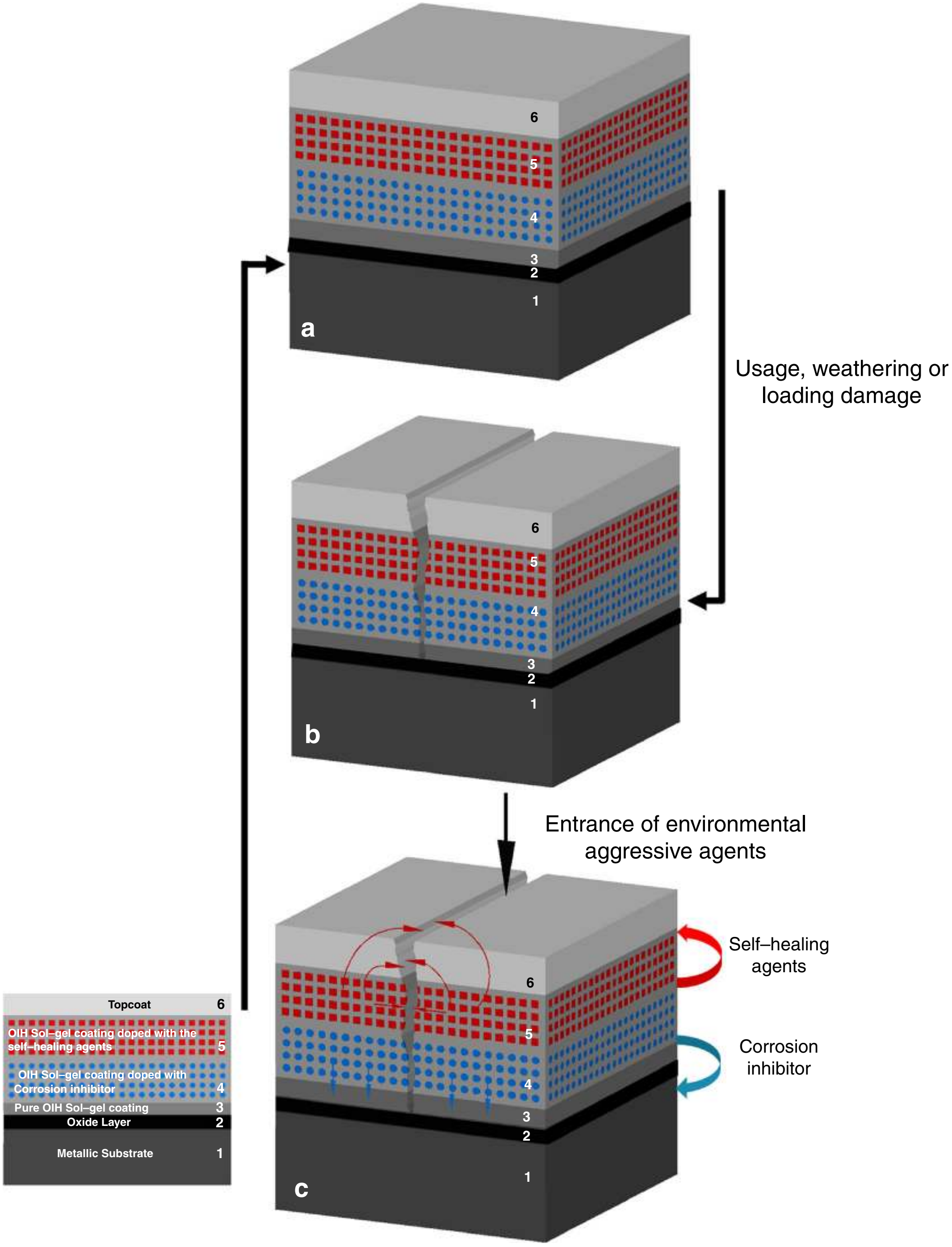


Fig. 16: (a) Multilayer coating system composed of five layers. 1—Metallic substrate; 2—oxide layer; 3—pure OIH sol–gel coating; 4—OIH sol–gel coating doped with a corrosion inhibitor; 5—OIH sol–gel coating doped with a self-healing agent; and 6—Topcoat. (b) Multilayer coating system after damage. (c) Expected behavior of the multilayer coating system behavior when in contact with exterior aggressive agents

self-healing agents dispersed within this OIH layer preserve their properties and mobility after the curing treatment. Finally, a highly hydrophobic topcoat layer should be deposited at mild conditions to combine the barrier effect protection and to avoid any possible degradation of the different OIH-based layers that are beneath. The total thickness of this type of multilayer coating system should be about 16 μm considering the use of dip-coating method that allows the production of each OIH layer with an average thickness of 4 μm. The schematic representation of the proposed multilayer coating system is displayed in Fig. 16.

Concluding remarks

Publications between 2001 and 2013 about OIH sol–gel coatings class II based on siloxanes, which were tested to prevent corrosion on metallic substrates, were reviewed. Since the early 1970s, academic interest in OIH materials has been accelerating and since the 1990s it has become a fast-growing and very complex subject with an almost exponential increase in the number of the scientific publications.

The main driving force in the development of OIHs class II based on siloxanes to prevent corrosion was the search for potential candidates to substitute environmentally unfriendly chromate surface treatments for metallic substrates.

The analysis of the papers published between 2001 and 2013 shows that it is on aluminum-based alloys where higher search efforts for an efficient coating to replace CCCs has been done, followed by steel substrates, zinc and magnesium alloys, with copper alloys in last place. Regardless of the type of substrate, the most frequently used precursors were GPTMS, TEOS, and TMOS.

Tested OIH materials present a large diversity of compositions and enhanced physical, mechanical, and morphological properties, among others. OIH materials show strong potential and are clearly becoming a reality as serious candidates for numerous applications such as smart coatings with "intelligent" self-healing properties and functional protective coatings. Moreover, the OIH sol–gel process shows high potential for the production of multilayer coating systems which are promising environmentally friendly candidates for replacement of the chromate-based pretreatments due to a synergistic effect of good barrier properties and effective "self-healing" action.

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