Methods of Modifying Anticorrosive Protective Properties of Silane Films

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Due to the fact that it is highly toxic and carcinogenic, chromate-based surface treatment is restricted or gradually reduced in many countries. Among the alternatives to replace conventional chromate coatings, organosilanes show some important advantages such as competitive price and environmental compatibility. These substances inhibit the corrosion processes of metal surfaces but cannot offer long term-protection. For this reason, silane films have been modified by different procedures. In this paper, methods of improving the anticorrosive protective performance of silane films have been presented.

1. Introduction

Corrosion is an undesirable natural process arising from the gradual destruction of materials, especially metals and their alloys, by chemical reaction with their environment, which causes huge energy and materials losses each year. Therefore, the study of preventing this phenomenon is very significant. One of the most active fields of research in the corrosion domain is focussed on developing new environmentally friendly and effective pretreatment systems. For a long time, chromate compounds (Cr^{6+}), exhibiting excellent anticorrosion properties, have been used as an effective and inexpensive surface treatment for various metals. Nowadays, due to their highly toxic and carcinogenic properties, their usage is restricted or gradually reduced in many countries. Among the proposed replacements, organofunctional silanes originally used as adhesion promoters have drawn special attention [1–5]. Silanes have the general formula $R\prime(CH_2)_nSi(OR)_3$, $R\prime$ being an organic functionality and RO an ethoxy (OCH_3) or methoxy (OC_2H_5) group, easily hydrolyzable in contact with water to silanol groups (SiOH) as shown in Fig. 1a [6]. Silanol groups adsorbed spontaneously onto a metal surface can react with metal hydroxide groups on the substrate surface and form an Si–O–Me covalent bonded film (Fig. 1b [6]) [7]. Unreacted silanol groups (SiOH) with different silane molecules undergo self-crosslinking and contribute to the formation of a siloxane (Si–O–Si) dense network limiting electrolyte access to the underlying metal and hence forming an effective barrier against corrosion (Fig. 1c [6]). Moreover, a thin silane coating promotes adhesion between the metallic substrate and other organic layers such as paints, varnishes, pre-treatment layers, and adhesives.

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Forming the silane film is a simple procedure achieved by dip-coating or the electrodeposition method [8]. The characteristics of the film formed on the metal and the protection afforded to the substrate depend on several variables such as the nature of the substrate, concentration, pH and temperature of the silane solution, as well as the way of application, and curing temperature of the film [8]. Organosilane base coatings have been successfully tested as anti-corrosion pretreatments on various metallic substrates such as: aluminum alloys [9, 10], magnesium alloys [11, 12], copper and their alloys [13, 14], galvanized [15–18], stainless [19, 20] and mild steel [21, 22] or NdFeB magnets [23].
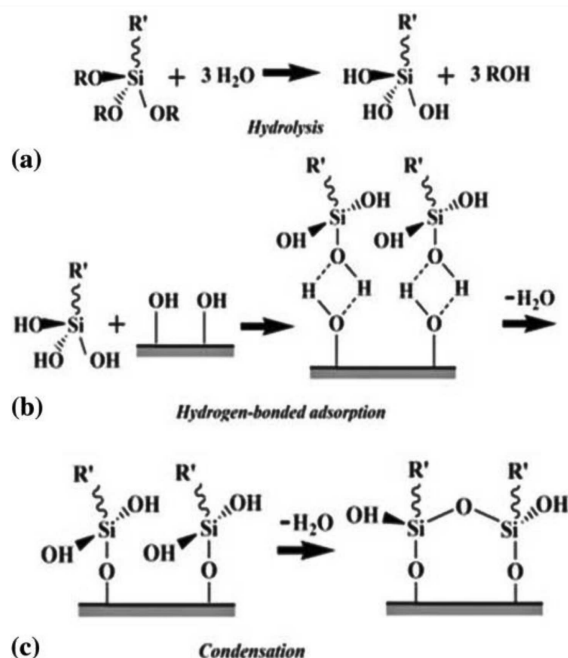

Fig. 1. Scheme of silane reactions (a) hydrolysis, (b) adsorption on metal, (c) condensation [6].

However, despite their beneficial properties, silane coatings are only a physical barrier and not able to ensure active inhibition of the corrosion process as well as chromate compounds do. Moreover, small defects (cracks, pinholes, areas with a low cross-link density) can be present in the silane coating through which corrosion initiators can diffuse to the coating/metal interface [24, 25]. Thus, in order to make the protecting performance of silane coatings more effective to corrosion processes, it is necessary to modify them. In this paper the methods of modifying the anticorrosive protective properties of silane films have been presented.

2. Modification of silane films with corrosion inhibitors

Chromate conversion coatings are able to seal small defects by forming trivalent chromium oxide at the damage site (self-healing capability). Pure silane films have no such useful properties. One of the ways to provide a self-healing ability and increase the corrosion resistance of silane films is to add corrosion inhibitors to them. Compounds of rare-earth elements, especially based on cerium salts (e.g. nitrates), are particularly interesting. Cerium is known to be an efficient corrosion inhibitor for many metals and alloys such as steel, aluminum and its alloys, magnesium and its alloys, as well as zinc alloys [26–30].

When a metallic substrate covered with modified silane film containing Ce^{3+} ions is immersed in an aggressive electrolyte, local destruction of the barrier silane coating immediately leads to contact of the solution with the metallic substrate and the corrosion process takes place. As is well known, corrosion reactions contain an anodic metal dissolution reaction and cathodic reduction reaction in the corroded areas of metals. At the cathodic sites a partial reaction of molecular oxygen reduction occurs according to the following reactions (1),(2) [31, 32]:

$$O_2 + 2H_2O + 4e^- = 4OH^-, \quad (1)$$

$$O_2 + 2H_2O + 2e^- = H_2O_2 + 2OH^-. \quad (2)$$
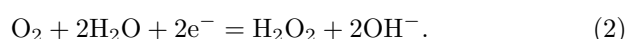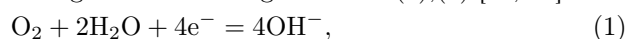
Due to H_2O_2 generation at the cathode, Ce^{3+} ions can be oxidized to Ce^{4+} ions [33, 34]. The presence of Ce^{4+} and Ce^{3+} in the silane film was confirmed by XPS measurements performed on galvanized steel substrates pre-treated with silane doped with cerium [35]. The Ce^{4+} oxidized form becomes trapped in the Si–O–Si network by substituting some Si atoms and forming an Si–O–Ce network [36–38] (Fig. 2), or they can be entrapped within the silane coating in the form of soluble species (cerium oxides/hydroxides).

The literature reports that cerium ions are mobile inside the silane film and can migrate to the active cathodic areas (a defect or scratch on the metal) [39]. The OH^- ions, the products from the cathodic sites, can interact with the Ce-ions and form cerium(III) and (IV) insoluble hydroxides and/or oxides by means of reactions (3),(4):
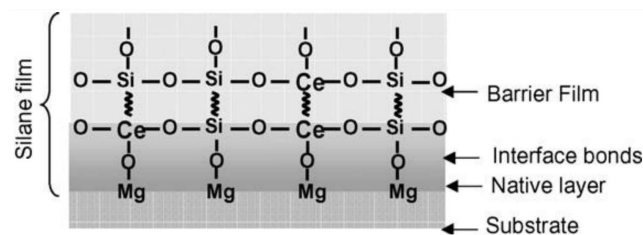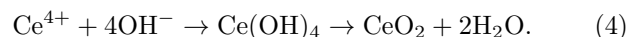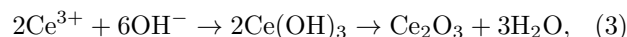

Fig. 2. Model of silane film structure doped with cerium ions [36].

$$2Ce^{3+} + 6OH^- \rightarrow 2Ce(OH)_3 \rightarrow Ce_2O_3 + 3H_2O, \quad (3)$$

$$Ce^{4+} + 4OH^- \rightarrow Ce(OH)_4 \rightarrow CeO_2 + 2H_2O. \quad (4)$$

Depositing these products on the cathodic sites greatly reduces the rate of the oxygen reduction reaction, hindering the transfer of electrons and consequently the entire corrosion process is blocked. The above mechanism can be used to explain the improved anti-corrosion behavior of metallic substrates pre-treated with silane solutions doped with cerium nitrate in comparison to sole silane layers. Montemor and Ferreira, who applied the scanning vibrating electrode technique (SVET), confirmed that cerium ions incorporated into a silane coating could inhibit corrosion processes at artificially damaged areas [36]. The improved corrosion resistance of the doped silane coatings suggests that the number of conductive pathways is much more reduced in the presence of the dopant. The literature reports that cerium-modified silane films were found to have improved barrier properties due to the reduced porosity and/or increased coating thickness, helping to decrease coating capacitance and increase coating resistance as well as self-healing ability provided by the presence of Ce^{3+} ions [35, 37]. The modification of silane coatings by adding cerium salts has been successfully tested for improvement in the corrosion protection of aluminum [39–41], zinc [42, 43], magnesium [44, 45] and mild steel substrates [46–48].

Silane films were doped with other rare earth salts such as lanthanum or zirconium nitrate. Trabelsi et al. [42] and Montemor [36] compared the inhibitive function of cerium nitrate and zirconium/lantanum nitrate in silane films. The results demonstrated that cerium ions are a more efficient dopant than zirconium or lanthanum. Silane coatings were also modified with such inorganic corrosion inhibitors as zinc salts or potassium permanganate. L.-K. Wu et al. [49] and Alinejad et al. [50] investigated the corrosion protection of mild steels by zinc-doped silane films. As evidenced by the obtained data, the addition of the inhibitor had no effect on the film thickness or condensation reactions. It was concluded that the superior corrosion protection in the presence of zinc cations arose from strengthening of the interface through depositing a compact layer which might be composed of zinc hydroxide and/or oxide on the mild steel surface. The tendency of zinc cations to deposit as hydroxide and oxide on the cathodic zones is reported

elsewhere [51]. The inhibiting and healing effects of potassium permanganate for silane films deposited on the AZ91D magnesium alloy substrate were evaluated by She et al. [52]. Scanning electron microcopy observations coupled with energy dispersive spectroscopy analysis (SEM/EDS) confirmed that $KMnO_4$ formed manganese oxide/hydroxide precipitates and blocked further propagation of the corrosion process. The results indicate that potassium permanganate would be a promising inhibitor for the silane film system and could have wide applications with its low price and high efficiency. The results of many works confirmed that the addition of corrosion inhibitors to modify silane coatings is beneficial up to a certain amount [45, 49, 50, 52]. It was verified that a higher than optimal corrosion inhibitor concentration in silane film caused a significant decrease in corrosion protection due to destabilization of the siloxane network. Thus, the presence of an optimal amount of active inhibitor creates an active corrosion protection ability of silane film and making it more efficient in inhibiting corrosion processes.

3. Modification of silane films with nanoparticles

Another important achievement in improving film growth and its corrosion performance was reported by doping silane films with nanoscaled inert particles, e.g. SiO_2 [53], CeO_2 [54, 55], and TiO_2 [56, 57], $CeO_2 \cdot ZrO_2$, [58], ZnO [59], Al_2O_3 [60]. Most of the authors confirmed that the presence of the nanoparticles increases the thickness of the silane layer and contributes to the blockage of conductive pathways through the silane layer, hindering the electrolyte uptake (pore blocking effect). This leads to a reduction in porosity and conductivity resulting in improved barrier properties compared to an unmodified silane coating. Silica nanoparticles are particularly attractive as dopants in silane films because a passivating silicate film may form on the metal and thus inhibit the cathodic reactions [61]. The results presented in work [62] demonstrated that CeO_2 nanoparticles in silane films due to their stability over a wide pH and the ability to form complexes with other species were found to provide superior barrier properties. Moreover, it is known that these nanoparticles inhibit the anodic reaction of the metal surface in the corrosion process [62]. Recently, silane films have been modified by carbon nanotubes and applied to 304 stainless steel by the dip-coating method [63]. Silane film doped with carbon nanotubes had better corrosion resistance than the plain silane coating. The carbon nanotubes may fill the pits and cracks in the silane film, effectively delay crack extension and densify the film (Fig. 3).
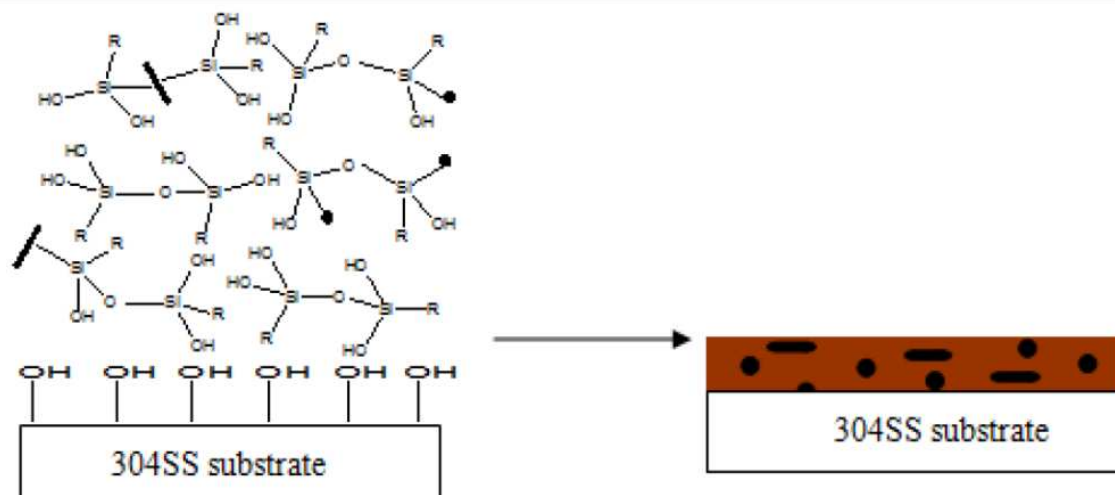

Fig. 3. Model of silane/carbon nanotubes coating [63].

One common conclusion in the reported results is that the addition of nanoparticles is advantageous up to a certain amount [53, 64, 65]. The optimum concentration of nanoparticles seem to be related to the size and type of nanoparticles, the silane type and the methods of nanoparticle incorporation in the silane solution. Nanoparticles incorporated into silane films at concentrations above their optimum resulted in the formation of a porous film which promotes electrolyte intrusion into the system, causing a premature film delamination process [61]. Furthermore, nanoparticle agglomeration may occur in the silane solution and the nanoparticles may not be homogeneously distributed in the film matrix. For this reason the silane film may still have cracks and pores that facilitate diffusion of the electrolyte to the metallic surface and thus the anti-corrosion performance is reduced [66]. Additionally, incorporating inorganic nanoparticles may also be a way to insert high amounts of corrosion inhibitor, preparing an inhibitor reservoir for self-repair pretreatments with controlled release properties [67]. Entrapped corrosion inhibitors become active in corrosive electrolytes in response to pH changes caused by

the corrosion process so that corrosion inhibitors slowly diffuse out of the host material. The literature reports that the combination of ceria nanoparticles and cerium ions [21] or silica nanoparticles and lanthanum ions [68] creates a synergistic effect that significantly improves the anticorrosive properties of silane films. The corrosion tests conducted by Zandi Zand et al. [58] suggest that activated CeO_2–ZrO_2 nanoparticles are more effective as nanostructured cerium ion reservoirs and can provide prolonged release of inhibitor ions.

One of the new concepts for modifying silane coatings is to incorporate sodium montmorillonite particles along with cerium nitrate as a corrosion inhibitor [69]. Such a film deposited on a pure Al substrate provided improved corrosion protection compared to the silane film, which is solely incorporated with nanoclay. The synergistic effect of the presence of nanoparticles and cerium ions could enhance the stability of the metal interface due to the montmorillonite particles, whereas the cerium component could enhance the coating performance thanks to the precipitation of cerium hydroxides and oxides on the metal surface.

4. Silane systems composed of different layers

Another possible way to improve silane coating properties is to use systems composed of different layers. Typically, in such systems the lower layer is to provide adherence to the metallic substrate and protection against corrosion, while the top layer complements the corrosion protection.

Recently Dun and Zuo [70] prepared a γ-(2,3-epoxypropoxy) propyltrimethoxysilane/graphene (GPTMS/rGO) coating on the AA-2024 aluminum alloy by immersing the aluminum alloy sample in a silane/graphene oxide solution. The graphene oxide was stacked layer by layer through the silanol groups. The GPTMS/rGO coating showed an excellent adhesion force, relatively high micro-hardness, good thermal shock resistance and excellent anti-corrosion performance. In a 3.5% NaCl solution the anodic current density of the aluminum alloy sample with the GPTMS/rGO coating was reduced by several orders of magnitude compared with those of the bare aluminum alloy or the sample with graphene film. Other authors [71] fabricated a polymethyltrimethoxysilane (PMTMS)/hydroxyapatite (HA) hybrid coating on a magnesium alloy by hydrothermal treatment and the immersion method. The results demonstrated that the corrosion resistance of the silane hybrid coating was significantly enhanced compared with the naked magnesium alloy. Moreover, the combination of HA and silane can provide functional groups for further immobilization of essential biological components to facilitate the development of biodegradable metallic implants [72, 73]. Another possible way to improve the corrosion protection afforded by silane layers is to use systems composed of silane and conducting polymers such as polypyrrole [74, 75] or polyrhodanine [76] on aluminium,

titanium, and stainless steel substrates, respectively. An electrochemical study and corrosion tests on samples coated with such bilayers coatings revealed that combination of both deposits yields a more protective structure with better corrosion resistance.

5. Other strategies used to modify silane films

It is worth adding that some other strategies like optimizing the curing time and temperature [9, 77], modifying some silane solution parameters such as pH [77], improving application methods [77–80], introducing silanes with a long aliphatic chain [81], and using silane mixtures [82] are important to modify the layer composition.

6. Conclusions

- The use of inhibitors in silane films provides them with a defect-healing capability, similar to that of chromate films.

- Incorporating nanoparticles improves the barrier properties of silane coatings as it may lead to the formation of crack-free films.

- The combination of nanoparticles and cerium ions creates a synergistic effect that significantly improves the corrosion inhibition capability of thin hybrid silane films.

- Adding corrosion inhibitors/nanoparticles to modify silane coatings is beneficial up to a certain amount. A higher than optimal corrosion inhibitor/nanoparticle concentration in silane film leads to poorer barrier properties and a reduction in corrosion protection.

- Silane films can be composed with other layers such as graphene oxide, conducting polymers, or hydroxyapatite to improve their protective properties.

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