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New architectured hybrid sol-gel coatings for wear and corrosion protection of low-carbon steel



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ABSTRACT

The replacement of expensive stainless steel in various socio-economic sectors such as mechanical or alimentary is an issue that would be possible to solve by developing a protective coating on low-carbon steel. In these applications, complex pieces are in contact with different kinds of fluids, with or without particles when functioning. Consequently, the expected coating function is to effectively protect the equipment from corrosion, abrasion and erosion.

In this work thin hybrid coatings obtained by the sol-gel process have been developed for corrosion and wear protection on low-carbon steel. This innovative system is constituted of alumino-silicate epoxy based sol-gel coatings acting as barrier layers which, when loaded with zirconia particles, improve the mechanical properties. Taking into account the specificity of the carbon steel, we developed two architectured coatings displaying corrosion and wear protection. They are built by superposition of a bi-layered hybrid primer coating and a mono-layered zirconia loaded hybrid coating. Using two different zirconia contents, 30 wt.% and 40 wt.%, thin coatings of 5 and 10 μ m are achieved. What is of interest is that the combination of antiwear tests and EIS to evaluate the influence of abrasive wear on anticorrosion properties has, for the first time, been demonstrated on such thin hybrid sol-gel coating. The loss of corrosion protection of material. On the contrary, the higher zirconia loaded coating demonstrated an interesting corrosion and wear behavior with the formation of a compacted layer at the top of the outer layer providing a barrier effect against water and ion permeation. To further characterize the protective systems, the morphology and the microstructure of the coatings were investigated by scanning electron microscopy.

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1. Introduction

Various protection systems are used for corrosion protection of mild steel. The use of organic coatings is one of the most common methods for corrosion protection of industrial components. According to the way they are applied, paints can cause environmental problems. This is the case of liquid paints containing volatile organic compounds the thickness of which range from 140 to 600 μ m depending on the corrosion requirements. Water-based paints are also developed but still contain a residual of solvent.

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To overcome environmental concerns, a powder coating process is used in the industry to coat and protect metal surfaces. The most commonly thermosetting resin powders used are polyesters, epoxy, epoxy polyesters [1–3]. These coatings are applied in one layer (60–80 μ m) or two layers (160–200 μ m) depending on the exposure conditions and the required durability. Recently, Montemor [4] described, in a review, different functional coatings and especially siloxane-modified epoxy coatings deposited on steel [5–7] which significantly improve conventional epoxy coatings properties. Another process used in industrial sectors is a protective thin layer electrodeposited [8] (15–25 μ m), but despite good corrosion resistance to salt spray test, additives present in the baths such as co-solvents and heavy metals can cause environmental problems.

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These protective systems present high thicknesses or even show limitations such as the presence of co-solvents, heavy metals or volatile organic compounds. A suitable technique to combine hard and pliant materials is the sol-gel process, where the hydrolysis and condensation reactions of inorganic alkoxides provide an inorganic network after appropriate thermal treatment. When organosilanes are involved in the process, a highly cross-linked network containing organic and inorganic parts is formed. These materials are of interest because they combine both properties of the organic polymer and the inorganic materials. The hardness and the flexibility of the coating can be adjusted by the amount of inorganic compounds (alumina, silica...) as well as polymerizable groups (e.g. epoxy, vinyl, methacrylate) for the formation of a dense network. Moreover the chemical compatibility with organic paints facilitates the adhesion of the coating to the substrate and the introduction of corrosion inhibitors such as cerium(III) salts improves coating performances against corrosion [9,10]. Finally, the hardness and mechanical resistance of the organic-inorganic hybrid coatings can be increased by nanoparticle reinforcement. Among the well-described coatings containing oxide nanoparticles which are essentially deposited on aluminum alloys, some papers deal with coated steel relating to different nanoparticles e.g. Zn [11], Montmorillonite [12], Al₂O₃ [13,14], ZrO₂ [15,16], SiO₂ [14,15,17,18] distributed in the hybrid matrix. The introduction of the nanoparticles within the hybrid sol may be done either as nanoscale powder [15], synthesized in-situ [16] or colloidal suspension [18].

The performance of a coating in an abrasion test depends on the intrinsic properties of the coating material as well as the film thickness and the adhesion of the sol-gel coating to the substrate. For example, the optimal amount of particles incorporated in the coatings clearly depends on its sol-gel matrix. This is highlighted by Grundwürmer et al. [19] who demonstrated that the addition of zirconia nanoparticles could either have a positive or negative effect on the erosion performances. Wilkes et al. [20]. explained that sol-gel coatings applied on various substrates, e.g. copper, brass and stainless steel are effective in wear control but have a poorer performance on the plain steel, due to a lower level of adhesion to the substrate.

The aimed protective coatings require good resistance to corrosion and abrasion. Indeed, mechanical damage can locally result in the reduction of the protective properties of a coating and, thus, a corrosion attack of the substrate might occur. Hence, the necessity to evaluate the resistance to the abrasion of the coating systems is achieved by abrasive wear tests. These tests have limitations in so far as they do not determine a precise value of the protective capacity, but they do allow the performance of comparative tests among the different coating systems. The most interesting abrasive wear test on coating is the Taber test [21], initially developed to evaluate the resistance of thick organic layers [1–3], and less applied to other sol-gel coated systems [16,20].

Wear and corrosion properties are usually independently investigated so that the influence of mechanical degradation on corrosion coatings performance is not well-correlated. During mechanical damage action, and taking thickness decrease and mass loss into consideration, as indicated in the standard, insufficient information can be extrapolated about the damage of the coating and its residual protective properties. In this sense, a test procedure has been developed to evaluate the decrease of protective properties by means of electrochemical impedance spectroscopy (EIS), after Taber Abraser standard test [1].

To date, particle-reinforced hybrid sol-gel coatings on corroding materials such as carbon steels have been poorly developed. One of the strategic issues of this technology is how the sol-gel can be formulated to obtain both high corrosion and abrasion resistant coatings on mild steel. This system should combine the barrier pro-

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Chemical composition of low-carbon steel (Fe balance).

Element	С	Mn	Ni	Cr	Mo
Mass%	0.047	0.26	0.010	0.016	≤0.005

tection effect of hybrid silicated and cerium doped coatings with the reinforcing action of nanoparticles.

The aim of this work was to design two innovative architectured systems combining bi- and monolayer coatings, the outer layer of which contains zirconia nanoparticles. Abrasion degradation of the architectured organic-inorganic sol-gel coatings caused by Taber Abraser was evaluated. Electrochemical impedance measurements and microstructural analysis were undertaken to evaluate the performance of the protecting systems. The two architectured systems have been compared and the best anticorrosive performances of such sol-gel coatings have been highlighted.

2. Experimental procedure

2.1. Sample preparation

The metal substrates are panels of low-carbon steel 100mm × 100mm × 1 mm the composition of which is given in Table 1. The metal substrates, after surface cleaning with acetone, were pre-treated following these two steps: 5 min immersion in NaOH, 1.125 mol L⁻¹ alkaline degreasing solution maintained at 60 °C to remove all traces of oil following by 5 min immersion in hydrochloric acid (5.5 mol L⁻¹) at room temperature in order to remove oxides or compounds on the surface of the sample and improve wettability. Samples are finally washed in ethanol and dried in air.

2.2. Sol and coating preparation

Glycidoxypropyltrimethoxysilane (GPTMS), aluminum isopropoxide (AIP, \geq 98%) and cerium nitrate hexahydrate (Ce (NO₃)₃,6H₂O) are obtained from Aldrich, polyethylene glycol PEG 35000 is obtained from Fluka, zirconia nanoparticles (TOSOH, 40 nm) were purchased from IMCD. The size of the TOSOH nanoparticles has been controlled by FEG-SEM observation. Zirconia nanoparticles were suspended in a 1:25 v:v water: isopropanol mixture. All others reagents were used as received.

S0 sol formulation of the primer layer was prepared by mixing GPTMS (5.94 g, 0.0251 mol) and AIP (3.6 g, 0.0176 mol) in a molar ratio of 1.7, in isopropanol 11.25 mL (0.1479 mol). Cerium nitrate hexahydrate (1.00 g, 0.0023 mol) was dissolved in distilled water (25.8 g, 1.43 mol) and then added to the previous mixture. The sol was prepared for a final volume of 46.1 mL. It was maturated during 24 h at room temperature. After maturation, the viscosity of the S0 formulation is 7 mPa.s.

For the S1 and S2 zirconia nanoparticles loaded sols, first GPTMS (9.52 g, 0.0403 mol) and AIP (2.4 g, 0.0118 mol)) in a molar ratio of 3.4, are mixed in isopropanol 7.5 mL (0.0986 mol). Aqueous solution of cerium nitrate hexahydrate (0.67 g, 0.0015 mol in 6 g, 0.33 mol of water, 0.05 mol L⁻¹) was added to the sol which is vigorously stirred. Then PEG 35000 (0.61 g) diluted in distilled water 6 mL) at a final concentration of 20 gL^{-1} was added to the sol. The sol was maturated during 24 h at room temperature and then X mL of sol was introduced in the zirconia suspensions containing 13.6 or 20.7 g in 25.9 mL of 1:25 v:v water:isopropanol to give S1 and S2 sols containing 30 wt.% and 40 wt.% of ZrO₂ nanoparticles, respectively. After maturation, the viscosity of the S1 and S2 formulations reaches 12 and 18 mPa.s respectively.

Two architectured coatings were produced by a dip-coating procedure at a controlled withdrawal rate of 20 cm min⁻¹. They were Download English Version:

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