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Mesoporous silica coatings with improved corrosion protection properties

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ABSTRACT

Sub-micrometer thin, compact and mesoporous silica coatings were prepared on Zn substrates by sol–gel method, aiming the replacement of traditional chromates conversion coatings and pretreatments. The effect of layer thickness, porosity and the character of pore structure, number of thermal treatments, and various silylating agents were studied on the anti-corrosion behavior of the coatings, systematically and comparatively. The surface-, structural-, and optical properties of various silica thin films were characterized with different methods thoroughly. The corrosion resistance of the coatings was comparatively evaluated by open circuit potential measurements, Tafel interpretation of the polarization curves, and electrochemical impedance spectroscopy. Thicker films have better anti-corrosion property, as expected. More interestingly, we show that porous layers can have such a good corrosion resistance as compact films. This fact has special importance when impregnation with inhibitor would be applied. Furthermore, rendering the coatings hydrophobic improves the corrosion resistance of both porous and compact coatings significantly. The character of pore structure, the type of silylating agents, and the thermal treatment applied between two consecutive dippings do not affect notably the protective properties of the silica films. Furthermore, we demonstrate the difference in the accessibility of the pores in the case of ordered and disordered pore structure.

1. Introduction

Galvanized steel is widely used in various industrial fields because of its mechanical and anti-corrosion properties. However, it still tends to corrode especially in aggressive environments, particularly in those containing industrial pollutants. Consequently, considerable efforts are being made to improve its corrosion resistance [1]. Chromate coatings are the most effective conversion coatings for galvanized steel, because of their self-healing nature and high corrosion resistance [2]. However, due to high toxicity of Cr(VI) salts, these conversion coatings are nowadays banished and efforts are made to replace them with other effective, but less toxic protective coatings [3–5]. One way to improve the corrosion resistance of Zn-coated steel by using chrome-free protective coatings consists in developing various silica- and titania-based layers on its surface. These inorganic coatings are widely used being a unique class of coatings that provide cathodic protection to ferrous and steel substrates, being environmental-friendly and exhibiting excellent barrier properties as anti-corrosive films. Moreover, they could successfully replace the conversion layers obtained by using Cr-containing solutions during post-sealing treatments of galvanized steel [6].

Sol–gel process is a convenient method for preparing different coatings on the surface of galvanized steel substrates. The main advantages of the sol–gel method are: (i) the possibility of preparation of materials with versatile composition, according to the requirements of application (ii) the availability to cast coatings in complex shapes, and (iii) the use of compounds that do not introduce impurities into the end product [6]. Silica-based protective coatings act very efficiently as corrosion protectors of metals under different circumstances [7–9]. Furthermore, due to the fact that using alkoxysilanes in the formation of silica precursors the reaction is quite gentle, this approach is extensively used in pretreatment of

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metal surfaces. It should be emphasized that the introduction of dopants, such as small amounts of nanoparticles (e.g. CeO_2, ZrO_2, etc., [10]) in the silica layer could significantly improve the barrier properties of the coatings, and, consequently, their corrosion resistance. Mesoporous sol–gel coatings and nanoparticles are suitable as inhibitor carriers for self-healing corrosion resistant systems [11–13]. For example, Borisova and co-workers prepared monodisperse, mesoporous silica nanoparticles loaded with corrosion inhibitor (1H-benzotriazole) and applied them embedded in hybrid SiO_x/ZrO_x sol–gel protection coatings with the thickness of ca. 2 μm on aluminum alloys [12]. Recently, novel results and trends were reviewed in this topic thoroughly by Montemor [13]. Silica based superhydrophobic sol–gel coatings are also promising for the prevention of metal surfaces against corrosion [7,8].

The objective of this study is to develop new silica-based coatings designed to produce an effective barrier, as well as, an appropriate support for passivity agents in corrosion protection of galvanized steel exploring the role and the effect of pore structure and silylation on protective property. For this purpose, compact and mesoporous silica coatings were prepared on Zn substrates by sol–gel method applying dip-coating technique. The role of layer thickness, porosity, thermal treatment, and various silylating agents was studied systematically and comparatively in the protective action towards corrosion. The effect of porosity and also the ordered or disordered character of pore structure is not trivial on the anti-corrosion behavior of the coatings in these material systems. Similarly, the impact of the thermal treatment applied between two consecutive dippings is also questionable on the pore structure and integrity of the coatings, thereby on the protective efficiency. Clarifying these details is crucial for further development of simple and cost-effective methods to produce self-healing inhibitor-impregnated coatings with outstanding anti-corrosion performance. In the case of water-soluble inhibitor materials the final silylation step is necessary to protect the inhibitor content of the pore system.

Silica coatings were obtained by using tetraethyl-orthosilicate as precursor, cetyltrimethylammonium bromide or Pluronic PE 10300 as templating agent in the case of porous layers, and finally dimethyldichlorosilane or trimethylchlorosilane as silylating agent. The surface properties were investigated by contact angle measurements and scanning electron microscopy. Structural properties were characterized by transmission electron microscopy and Ellipsometric Porosimetry. The optical properties of the silica thin films were measured by UV–Vis spectroscopy (on glass substrates), and the main parameters – such as layer thickness, refractive index, and porosity – were determined by appropriate optical modeling. The anti-corrosion performance of the coatings was characterized by open circuit potential measurements, Tafel interpretation of the polarization curves, and electrochemical impedance spectroscopy.

2. Experimental

2.1. Materials

Tetraethyl-orthosilicate (*TEOS*, for synthesis, >99%, Merck), ethanol (*EtOH*, a. r., >99.7%, Reanal), hydrochloric acid (*HCl*, purum, 37%, Fluka), and distilled water (18.2 MΩ cm, purified with a Millipore Simplicity 185 filtration system) were used as starting materials for silica (SiO_2) precursor sol synthesis. In order to prepare mesoporous silica coatings cetyltrimethylammonium bromide (*CTAB*, cationic surfactant, 99+%, Acros Organics) or Pluronic PE 10300 triblock copolymer (*Pluronic*, non-ionic surfactant, BASF, Ludwigshafen Germany) templates were used during precursor sol synthesis.

Dimethyldichlorosilane (*DMDClSi*, >99%, for analysis, Merck) or trimethylchlorosilane (*TMClSi*, 98%, Nitrogen flushed, Acros Organics) solutions in n-Hexane (>99%, for analysis, Merck) were applied as silylating agents. The impregnation experiments were carried out using Rhodamine 6G (*R6G*, ~95%, Sigma–Aldrich) dye. Sodium sulfate (Na_2SO_4, 99%, Riedel-de Haën, Germany) was used during electrochemical measurements and at a part of wettability and dye release investigations. Hydrochloric acid (*HCl*, purum, 37%, Fluka) and distilled water (18.2 MΩ cm, purified with a Millipore Simplicity 185 filtration system) were also applied during dye release experiments.

Zinc wafers (*Zn*, 76 × 26 × 0.65 mm, Bronzker Bt, Hungary), silicon (*Si*) wafers and microscope glass slides (76 × 26 × 1 mm, Thermo Scientific, Menzel-Gläser) were used as solid substrates of the coatings. Substrates were cleaned before layer deposition by using the following materials: hydrochloric acid (*HCl*, purum, 37%, Fluka, in the case of *Zn* substrate), 2-propanol (*2-PrOH*, a. r., >99.7%, Reanal) and distilled water (H_2O, 18.2 MΩ cm, purified with a Millipore Simplicity 185 filtration system).

2.2. Synthesis of precursor sols

Silica precursor sols were prepared by an acid catalyzed, controlled hydrolysis of tetraethyl-orthosilicate in ethanolic media. 0.1 M aqueous solution of hydrochloric acid was used as catalyst.

Precursor sol K was synthesized for depositing compact silica (*K*) sol–gel coatings. The molar ratios for *TEOS*:*EtOH*:H_2O:*HCl* were $1:18.6:5.5:1 \times 10^{-3}$, and the mixture was stirred for 1 h at room temperature.

Porous silica (*C* and *P*) coatings were prepared from precursor sols (*precursor sol C* and *precursor sol P*) containing surfactant (*CTAB* or *Pluronic*) templates.

Precursor sol C and *precursor sol P* were prepared by dissolving 1.5 g of *CTAB* and 2 g of *Pluronic* triblock copolymer in 22 mL of *EtOH*, similarly as in Ref. [14]. Please refer to Table 1.

In both cases *EtOH*, *TEOS* and 0.1 M *HCl* were mixed in another beaker applying the same molar ratios as for the preparation of *precursor sol K* with the total volume of 35 mL. Both mixtures were stirred for 30 min at room temperature and for additional 30 min after mixing the two solutions.

Table 1
Summary of sample preparation and the used symbols (Pluronic: Pluronic PE 10300; CTAB: cetyltrimethylammonium bromide; DMDClSi: dimethyldichlorosilane; TMClSi: trimethylchlorosilane).

Symbol	Type of sample/templating agent	Number of consecutive applications of the dip-coating method	Thermal treatment	Silylating agent
K4	Compact SiO_2/–	4	After the final dipping	–
K4D				DMDClSi
K4T				TMClSi
K2		2		–
K2D				DMDClSi
K2T				TMClSi
K2HD			After each dipping step	DMDClSi
K2HT				TMClSi
P2	Porous SiO_2/Pluronic	2	After the final dipping	–
P2D				DMDClSi
P2T				TMClSi
P2HD			After each dipping step	DMDClSi
P2HT				TMClSi
C2	Porous SiO_2/CTAB	2	After the final dipping	–
C2D				DMDClSi
C2T				TMClSi
C2HD			After each dipping step	DMDClSi
C2HT				TMClSi