Silica sol – gel protective coatings against corrosion of zinc substrates

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1 Introduction

The need to replace the harmful chromate-based surface treatments of galvanised steel with environmentally friendly methods promoted the development of new treatments based on electropolymerization [1], conversion coatings [2-5] and sol-gel synthesis [6,7,8]. Among these, the sol-gel coatings for corrosion protection of metals are considered a promising alternative due to their easy preparation at low temperatures and to the possibility to incorporate various additives and/or nanoparticles in order to control the physical and chemical properties of the coatings [9,10].

Layers of oxides such as SiO₂, ZrO₂, Al₂O₃, TiO₂, CeO₂, etc. provide effective protection to metal substrates due to their very good chemical and thermal stability. Among them, SiO₂ layers act very efficiently as corrosion protectors of metals under different temperatures. Moreover, due to the fact that using alkoxysilanes as precursors in the formation of silica sol-gels the reaction is quite gentle, this approach is extensively used in pretreatment of metal surfaces [6]. It should be emphasized that the introduction of dopants, such as small amounts of nanoparticles (e.g. CeO₂, ZrO₂ [10] etc.) in the SiO₂ layer could significantly improve the barrier properties of the coatings and, consequently, their corrosion resistance. Moreover, properties of SiO₂ sol-gel coatings and nanoparticles can be influenced by using different surfactants during the preparation process [11].

Zinc has found widespread use as the basis of a whole range of sacrificial coatings for ferrous substrates. However, the life span of such coatings is limited due to the aggressive nature of some environments, particularly those containing industrial pollutants. Consequently, efforts are made in order to enhance their service life.

In this context, our investigation was focused on the preparation and characterization of different type of porous and compact silica-based protective coatings on zinc and glass substrates by using sol-gel method, in the absence or in the presence of surfactants. The optical and the electrochemical properties of the coatings, as well as the effect of film thickness on its protection ability were also studied.
2 Experimental

2.1 Synthesis of precursor sols

Three different types of silica precursor sols were prepared by the acid catalyzed, controlled hydrolysis of tetraethyl-orthosilicate (TEOS, >99%, Merck) in ethanolic media (EtOH, a. r., >99.7%, Reanal). Hydrochloric acid (HCl, purum, 37%, Fluka) was used as catalyst and it was added together with water as a 0.1 M aqueous solution.

Precursor sol (1) was synthesized for depositing compact silica sol-gel (compact SiO₂) coatings. The molar ratios for TEOS: ethanol: water: HCl were 1: 18.6: 5.5: 1x10⁻³, and the mixture was stirred for 1 h at room temperature [12].

Porous silica (CTAB/porous SiO₂, and Pluronic/porous SiO₂) layers were prepared from precursor sols (precursor sol (2) and precursor sol (3)) containing surfactant templates.

Precursor sol (2) and precursor sol (3) were prepared by dissolving 1.5 g of cetyltrimethylammonium bromide (CTAB, cationic surfactant, 99%, Acros Organics) and 2 g of Pluronic PE 10300 triblock copolymer (non-ionic surfactant, BASF, Ludwigshafen Germany) in 22 mL of ethanol respectively.

In both cases ethanol, TEOS and 0.1 M HCl were mixed in another beaker applying the same molar ratios as for the preparation of precursor sol (1) 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.

2.2 Preparation of coatings

For layer deposition processes zinc wafers and – for comparison – microscope glass slides (76x26x1 mm, Thermo Scientific, Menzel-Gläser) were used as solid substrates.

Prior to film deposition, zinc substrates were polished with emery paper (grade 2000) then treated with 0.1M HCl solution and rinsed with 2-propanol (a. r., >99.7%, Reanal).

Glass slides were erased with 2-propanol impregnated cotton, then rinsed with 2-propanol and distilled water (18.2 MΩ·cm, purified with a Millipore Simplicity 185 filtration system). Both glass and zinc substrates were dried at room temperature before using.

Sol-gel films on glass and zinc substrates were prepared from the precursor sols by the dip-coating method (dip coater, MTA TTK MFA, Hungary). Cleaned and dried substrates were immersed into the precursor sol and pulled out with a constant speed. Withdrawal speeds were 10 cm/min for compact SiO₂ and CTAB/porous SiO₂ and 8 cm/min for Pluronic/porous SiO₂ film deposition. Multilayered coatings were obtained by the consecutive application of the dip-coating method.

The deposited films were annealed in a drying oven (Nabertherm B170) at 450°C (glass substrate) and 410°C (zinc substrate) for 1 h with a heating rate of 20°C/min. In the case of multilayered coatings prepared onto glass slides heat treatment was applied after each layer deposition. In order to spare the surface of Zn substrate in case of multilayer deposition annealing was carried out only after the final layer formation.

2.3 Optical characterization of coatings

Optical properties of mono- and multilayered coatings on glass substrates were measured by UV-Vis spectroscopy. Transmittance spectra of the bare substrates and coatings were taken using a Specord 200-0318 spectrophotometer in the wavelength range of 350-1100 nm with 1 nm resolution and a scanning speed of 5 nm/s.

The obtained transmittance curves were analyzed in terms of thin layer optical models. Transmittance spectra of coatings were fitted with a homogeneous layer model [13] supposing perpendicular angle of incidence and identical homogeneous monolayers on both sides of the transparent substrate. The fitting procedures provided effective refractive index and film thickness values. As the glass substrate had weak absorption, the transmittance spectra were corrected before fitting to eliminate the effect [13,14]. The fitting procedure used a Levenberg – Marquardt algorithm [15]. Porosity of coatings was estimated using the Lorentz-Lorenz formula [16,17,18].

2.4 Characterization of coatings by SEM

Surface morphology of the emery paper, of the polished zinc substrate and selected samples (two layered compact SiO₂, four layered CTAB/porous SiO₂ and four layered Pluronic/porous SiO₂) prepared onto zinc substrates were investigated by scanning electron microscopy. Overview images were taken using a JEOL JSM 6380LA scanning electron microscope. The samples were sputtered by Pd/Au alloy (JEOL gold coater).

2.5 Electrochemical investigations

Electrochemical investigations were carried out in a three-electrode cell containing a working electrode (pure Zn and SiO₂-coated samples, S = 2 cm²), a counter electrode (platinum wire), and a reference electrode (Ag/AgCl/KCl). All corrosion measurements were performed in 0.2 g/L aqueous solution (pH=5) of Na₂SO₄ (Riedel-de Haën, Germany). Measurements were carried out with a computer-controlled potentiostat AUTOLAB, PGSTAT302N (Eco Chemie BV, Utrecht, Netherlands) and GPEs program was used for data analysis. In each case, before the polarization measurements, the open circuit potential (OCP) was recorded during 1 hour, until it was stabilized. The corrosion potentials and the corrosion current densities were estimated by using Tafel plots.

3 Results and discussion

3.1 Optical properties of mono- and multilayered coatings

For characterization of coating samples, optical model investigations were carried out. Transmittance spectra were taken from uncoated glass substrates and from all types of mono- and multilayered silica coatings prepared on glass substrates.
All the prepared silica sol-gel layers had higher transmittance than their bare substrates for the whole studied wavelength range (Figure 1 a), b) and c)) and the highest transmittance was found for Pluronic templated coatings. Film thickness and effective refractive index values resulted from the fitting procedures were collected in Table 1. The reduced chi-square values of the fitting were in the range of $10^{-7}$ - $10^{-8}$, and the coefficient of determination ($R^2$) value was above 0.995 which indicated a good agreement between measured and calculated spectra.

Porosity values calculated in view of effective refractive index of the layers and refractive index of the bulk silica ($n_{\text{bulk}} = 1.450$) and air ($n_{\text{air}} = 1$) are also listed in Table 1. Thickness value of 2 layered compact silica coating (136 ± 5 nm) is commensurable with that of 1 layered CTAB/ porous silica (136 ± 2 nm) and Pluronic/porous silica (124 ± 3 nm) coatings, while layer thickness of 4 layered compact silica (251 ± 2.5) with thickness of 2 layered porous coatings (198 ± 6 nm and 219 ± 2 nm for CTAB and Pluronic templated silica coatings respectively). As can be seen the Pluronic template is more effective for increasing porosity.

3.2 Characterization of surface morphology by scanning electron microscopy (SEM)

SEM images were taken from the emery paper (Figure 2) used for smoothing the surface of Zn substrates, from the surface of the polished Zn substrate (Figure 3) and from the multilayered coatings with commensurable layer thickness values, deposited onto the polished Zn surfaces: 4 layered compact silica coating (Figure 4), 2 layered CTAB/porous silica and 2 layered Pluronic/silica coatings (Figure 5 and Figure 6 respectively). Figure 3 shows that the surface of the polished, bare Zn substrate still has stripe - type unevenness. Similar surface pattern was also observed in the case of coated surfaces (Figure 4, Figure 5 and Figure 6). It means that the investigated sol-gel coatings cannot flatten out completely the metal surface. As can be seen in case of four - layered silica (Figure 4) a special cracking - type pattern superposes onto the original one.

3.3 Electrochemical properties of coatings deposited onto Zn surfaces

The polarization tests carried out in a potential range of ± 20 mV vs. OCP were used to determine the polarization resistance ($R_p$) of zinc and of SiO$_2$-coated zinc samples from the slope of the linear $E$=$f$(i) curve, and the results are presented in Table 2.

It can be observed that the uncoated Zn has the most negative OCP value and that a positive shift of the OCP is noticed in the case of all SiO$_2$ coated samples, suggesting that these samples acquired more noble character and thus, an increased corrosion resistance.

On the other hand, the uncoated Zn samples exhibit the lowest $R_p$ value, while the highest $R_p$ value is recorded in the case of the zinc sample coated with 2 porous layers of SiO$_2$ prepared in the presence of CTAB. This proves the protection ability
of the SiO₂ layers and points out to the importance of the preparation method and of the ingredients used for the obtaining of sol-gel coatings.

In Figure 7 a), b) and c) the electrochemical response of different SiO₂ coated Zn samples are compared with that of uncoated zinc. The polarization curves were recorded in a ± 200 mV potential range around the OCP. The Tafel plots were used to extract the corrosion potential \(E_{corr}\), the corrosion current density \(i_{corr}\) and the Tafel slopes values. The obtained results are presented in Table 3.

| Sample                  | OCP [V vs. Ag/AgCl] | Rp [Ωcm²] | R/N       |
|-------------------------|---------------------|-----------|-----------|
| Zn                      | -0.994              | 98.5      | 0.9991/ 28|
| compact SiO₂, 2 layers  | -0.934              | 1649.3    | 0.9996/ 50|
| compact SiO₂, 4 layers  | -0.927              | 1804.0    | 0.9990/ 27|
| CTAB/porous SiO₂, 1 layer | -0.948             | 709.2     | 0.9992/ 24|
| CTAB/porous SiO₂, 2 layers | -0.910             | 2147.3    | 0.9990/ 27|
| Pluronic/porous SiO₂, 1 layer | -0.956              | 900.9     | 0.9993/ 22|
| Pluronic/porous SiO₂, 2 layers | -0.943             | 1633.0    | 0.9992/ 25|
It can be observed that the corrosion current density of the coated samples decreased with an order of magnitude in comparison with the uncoated Zn samples and the polarization resistance increased correspondingly. This effect could be correlated with the physical properties of the coatings, which act as a barrier between the corrosion medium and the zinc substrate.

The protection efficiency increases with the number of layers. As expected, multilayered coatings are more efficient than single ones and the porous coatings provide better protection than compact ones. The reason for the unexpected efficiency of the porous layers can be due to an improved coating ability (wettability) of precursor sols containing surfactants as compared with the precursors without surfactants which were used for the preparation of the compact layers. It is worth mentioning that the layers prepared from precursor sols templated with CTAB were more efficient than those prepared from sols containing Pluronic PE 10300. This behaviour can be attributed to different porous structures and porosities.

4 Conclusions

Based on the above-mentioned results, some conclusions can be drawn:

- all SiO$_2$ coatings provided corrosion protection to zinc
- the open-circuit potentials of the SiO$_2$ coated samples are more positive than for pure Zn, and the corrosion current density on the coated samples decreased with an order of magnitude, proving the protection ability of the SiO$_2$ layers
- multi-layered coatings are more efficient than single ones and the porous coatings provide better protection than compact ones
- the layers prepared from precursor sols templated with CTAB were more efficient than those prepared from sols containing Pluronic PE 10300 as a result of different porous structures and porosities
- the reason for the unexpected efficiency of the porous layers can be an improved coating ability of precursor sols containing surfactant due to the better wetting ability of surfactant solutions

The interpretation of the experienced effects requires further investigations that are in progress in our laboratories.

### Tab. 3. Corrosion parameters extracted from Tafel plots for uncoated Zn and SiO$_2$ coated samples ($i_{corr} =$ corrosion current density, $E_{corr} =$ corrosion potential, $b_a =$ anodic activation coefficient, $b_c =$ cathodic activation coefficient, $v_{corr} =$ corrosion rate)

| Sample                        | $i_{corr}$ [A/cm$^2$] | $E_{corr}$ [V vs. Ag/AgCl] | $b_a$ [V$^{-1}$] | $b_c$ [V$^{-1}$] | $v_{corr}$ [mm/year] |
|-------------------------------|------------------------|-----------------------------|------------------|------------------|----------------------|
| Zn                            | $1.215 \times 10^{-5}$ | -0.996                      | 0.020            | 0.036            | $1.81 \times 10^{-1}$ |
| compact SiO$_2$, 2 layers     | $1.819 \times 10^{-6}$ | -0.859                      | 0.029            | 0.026            | $2.712 \times 10^{-2}$ |
| compact SiO$_2$, 4 layers     | $1.871 \times 10^{-6}$ | -0.896                      | 0.031            | 0.021            | $2.789 \times 10^{-2}$ |
| CTAB/porous SiO$_2$, 1 layer  | $2.76 \times 10^{-6}$  | -0.924                      | 0.024            | 0.031            | $4.115 \times 10^{-2}$ |
| CTAB/porous SiO$_2$, 2 layers | $1.087 \times 10^{-6}$ | -0.859                      | 0.018            | 0.013            | $1.62 \times 10^{-2}$ |
| Pluronic/porous SiO$_2$, 1 layer | $3.832 \times 10^{-6}$ | -0.948                      | 0.046            | 0.025            | $5.713 \times 10^{-2}$ |
| Pluronic/porous SiO$_2$, 2 layers | $1.207 \times 10^{-6}$ | -0.905                      | 0.021            | 0.022            | $1.799 \times 10^{-2}$ |

Fig. 7. Tafel plots of the polarization curves recorded for uncoated Zn substrates (circles) and for different type silica coatings: a) compact silica coatings (2 layers: squares, 4 layers: triangles); b) porous SiO$_2$ sol-gel coatings templated with CTAB (1 layer: squares, 2 layers: triangles); c) porous SiO$_2$ sol-gel coatings templated with Pluronic PE 10300 (1 layer: squares, 2 layers: triangles) (i = current density, E = potential).
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