ON THE ANTICORROSIVE SiO₂ SOL GEL COATINGS ON STEELS. A REVIEW

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Abstract. This article summarizes the results obtained by the authors from the preparation and investigation of anti-corrosion oxide layers synthesized by sol-gel technology. Included results are based on the protective properties of SiO₂ thin films. ZrO₂, CeO₂, TiO₂, and Nd₂O₃ thin films are deposited on SiO₂ films by dip coating to obtain multilayer coatings. X-ray diffraction, scanning electron microscopy, energy-dispersive X-ray, atomic force microscopy, X-ray photoelectron spectroscopy, and NaCl weight loss test have been applied to study the new anti-corrosion oxide layers. The obtained multilayer structures of SiO₂/TiO₂ SiO₂/CeO₂, SiO₂/ZrO₂ are promising with the view to increase the corrosion resistance of the steel. It has been revealed that Nd₂O₃ doped silica coatings can provide a higher chemical resistance.

Keywords: sol-gel, anticorrosion, dip coating, SiO₂.

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1. INTRODUCTION

The corrosion control of metals is of economical, technical and environmental importance. Corrosion processes are accompanied by a number of reactions that change the composition and properties of the metal surface, and can be reduced through the selection of appropriate materials for particular application, like new alloys, corrosion inhibitors or protective films and coatings deposited onto the metal surface, especially in aggressive environments. Oxide films and coatings such as SiO_2 , ZrO_2 , Al_2O_3 and TiO_2 can be deposited on metals to improve their surface and anticorrosion properties [1–6]. There are different methods of obtaining thin films and coatings on metal surface, namely: electrochemical deposition [7], Physical Vapor Deposition (PVD) [8], Chemical Vapor Deposition (CVD) [9], plasma spraying [10], and sol-gel process [1, 5, 11–16]. The advantages of sol-gel technique are: low processing temperature, good homogeneity, use of compounds that do not introduce impurities into the end product as initial substances, preparation of nano-sized materials, significant decreasing of sintering temperature, and enhancement of the reactivity of prepared compounds. The cost of precursor solutions has limited the use of sol-gel processing in many applications [17]. The sol-gel method is a wet chemical technique and involves several stages: hydrolysis and polycondensation, gelation, aging, drying, densification and crystallization. The sol-gel technology is based on the hydrolysis and condensation reactions [18, 19]. Typically, the addition of catalysts (HNO_3 , HCl , CH_3COOH) increases the hydrolysis rate. The type of catalyst determines the pH of sols and affects the form of sol-gel materials, i.e. obtaining the films, powders or monoliths. The pH value of the reaction mixture, which is dependent on the used catalyst, influences the hydrolysis and condensation reaction, and affects the form and structure of the obtained materials. One of the most technologically important aspects of sol-gel processing is the ability to produce coatings with sintering temperatures lower than 500°C . The structure of sol-gel coatings may undergo changes depending on heat treatment conditions, especially the final treatment temperature. A sol-gel coating can be applied to a metal substrate through two techniques: dip-coating or spin-coating [11, 12]. The proper selection of synthesis parameters and the way of preparing materials are significant of the successful sol-gel synthesis. These advantages make the sol-gel process one of the most appropriate technologies for preparation of thin, nanostructured films. The sol-gel process gives possibilities to obtain coatings with unique diffusion, abrasion, dielectric etc. properties [17]. The preparation of coating by means of sol-gel method is an established method of producing homogeneous coatings with uniform thickness below $2\text{ }\mu\text{m}$ [20]. Sol-gel technology has been

significantly improved in the past 20 years. The sol-gel coatings are widely investigated and applied in the area of optics [21], nano bio-composites [22], biomaterials [23], self-cleaning materials [24] and others [25]. Different sol-gel coatings have been developed to increase the corrosion resistance of metals, although the pure inorganic films have limitations such as micro cracks, residual porosity and thickness [26, 27]. Coatings with good passivity, insulating properties, and good tribological properties show high corrosion resistance in aggressive environment. Some papers [28–31] have showed the feasibility of obtaining homogeneous and free of cracks sol-gel coatings on steel substrates. Another work [32] has demonstrated increase in the corrosion resistance of steel sheets by using zirconia or silica coatings.

The sol-gel method is considered to be an effective method of obtaining oxide films due to low deposition temperatures and the possibility of mixing raw materials at molecular level [33]. When obtaining sol-gel coatings from SiO_2 , metal alkoxides undergo first hydrolysis and then polymerization. The films are then deposited by using two techniques: immersion or centrifugation, then deposits are converted into an oxide layer by heating. It is known that the treatment temperature is the main factor influencing the oxidation of the metal substrate [34]. However, the evidence for this influence in literature is opposite. Vasconcelos *et al.* have demonstrated that treatment at 200°C results in greater corrosion resistance to SiO_2 films than that of heat treated at 80°C due to the lower concentration of hydroxyl groups [35]. Another research group has studied the corrosion resistance of SiO_2 coatings to stainless steel heat treated at higher temperatures. The effect of the time of heat treatment of the SiO_2 films on the corrosion resistance of stainless steel in 15% H_2SO_4 is studied through potentiodynamic polarization curves at 25°C [36]. On the other hand, the microstructure and density of silica films are highly dependent on the composition of the sol [37]. Therefore, the optimal combination between the concentration of precursor sol and the processing temperature is a key factor in obtaining SiO_2 coatings with good protective properties.

The purpose of this study is to perform a review of the effect of certain deposition parameters of SiO_2 protective films on their surface structure after a corrosive attack in a NaCl solution. Therefore, we try to find experimentally the relationship between the concentration of Tetraethyl Orthosilicate (TEOS), processing temperature, surface structure and anti-corrosion properties of SiO_2 coatings obtained by means of sol-gel method.

2. SiO₂ MULTI-LAYER COATINGS

2.1. Experimental part

The preparation procedure of SiO₂ films by means of the sol-gel method is as follows: TEOS is dissolved into ethanol and stirred for 1 h [39]. The mixture of ethanol, water and hydrochloric acid is added to the TEOS solution, and then also stirred for 2 hours in order to obtain 0.5M and 2M solutions. The mole ratio H₂O:TEOS is 3.7. The sample obtained from 0.5M solution is denoted A, while the sample deposited from 2M solution is denoted B. The stainless plates AISI 316 are used as substrates. The substrates are cleaned ultrasonically in ethanol and acetone. The films are immersed in the corresponding solution and withdrawn at a constant rate of 3 cm/min, and then dried consequently at 60 °C and at 90 °C. The samples A and B are heated at 300 °C. These steps are repeated 3 times. Another sample denoted C produced from 2M solution is treated at 500 °C for 1 h to study the effect of thermal treatment temperature on the protection properties. The phase composition of the samples is studied by X-ray Diffraction (XRD) with CuK α -radiation (Philips PW 1050 apparatus). The average crystallite sizes of the films are estimated according to Scherer's equation. The morphology of the coatings is investigated by means of Scanning Electron Microscope (SEM) PHILIPS 515, Belgium, operating at 20 kV. The investigated samples, as well as uncoated steel (reference sample), were exposed to the action of solution of 3.5% NaCl at 25 °C (7EN ISO10289/2006) in the course of 346 hours to study their chemical resistance [40]. The solution temperature and the air temperature are controlled by calibrated thermometers. The mass weight loss is determined after 256 and 346 hours.

2.2. Results and discussion

XRD analyses reveal that all the samples are amorphous, since no signals of crystallized SiO₂ are observed. A research group has obtained amorphous silica coatings, thermally treated at 1000 °C [41]. Another research group also has obtained silicon dioxide, which is in an amorphous state even after heat treatment at 900 °C [42]. The surface composition and chemical state of the SiO₂ layers are investigated by X-ray Photoelectron Spectroscopy (XPS). XPS analysis represents peaks of O1s, C1s and Si2p on the surface of the films, as it can be seen from the spectra, Fig. 1(a). The Si2p peak has a maximum at 103.8 eV typical of Si⁴⁺ oxidation state, and it is in agreement with literature sources relevant to the single oxide [43], Fig. 1(b). The O1s peak at 533 eV is

Fig. 1. XPS analysis presents peaks on the surface of the films:
(a) O1s, C1s, Si2p; (b) Si2p; (c) O1s

attributed to lattice oxygen in SiO_2 , Fig. 1(c). The chemical composition of the SiO_2 film is estimated as follows: 28.1 wt% silicon and 71.9 wt% oxygen.

The typical Energy-Dispersive X-ray (EDX) spectrum of sample A indicates the presence of both Si and O peaks, Fig. 2. As shown in the EDX analysis, the appearance of various prominent peaks for Cr, Mn, Ni and Fe confirms the presence of these elements, which are characteristic of the steel substrate. The measurements are performed in four different locations of the same sample, and the results confirm that the quantities of O and Si in all points are identical.

Fig. 2. The typical EDX spectrum of sample A

Fig. 3. SEM image of stainless steel substrate, comparing the bare substrate surface with the surface after corrosion attack

The average concentrations of silicon, oxygen, chromium, manganese, nickel and iron are 19.74; 54.5; 5.41; 0.35; 18.14 and 1.84 wt%, respectively.

We have applied both SEM and Atomic Force Microscopy (AFM) analyses as non-destructive tools in order to study the submicron changes in the structural properties of SiO_2 sol-gel films caused by corrosive attack. Figure 3 shows the SEM image of stainless steel substrate, comparing the bare substrate surface with the surface after corrosion attack, Fig. 3(a). It is visible that the surface of the stainless steel has been undergone considerable changes during the corrosion test. Deep cracks are clearly visible, Fig. 3(b). The surface coated with silica films prepared from 0.5M TEOS solution is relatively dense with some unevenness, Fig. 3(c). The morphology becomes more flat, when higher concentration of TEOS solution is applied for deposition, regardless of the temperature of the final treatment, Fig. 3(d).

Figure 4 represents the AFM photographs of the surface of SiO_2 coating after corrosion attack. Sample A has not any visible cracks after corrosive

Fig. 4. AFM images of the surface of SiO₂ coating after corrosion attack:
 (a, c) 3D images; (b, f) 2D images; (d) 3D with cross-section;
 (e) 2D with cross-section

test, Fig. 4(a). The surface defect seen in Fig. 4(a) can be a result from the mechanical stress during the process of cutting, and could be denoted as mechanical indentation. The roughness analysis gives the value R_a about 15 nm and R_q 24 nm for sample A after the corrosion attack, Fig. 4(b). With ongoing corrosion, the surface of the films obtained from 2M TEOS solution displays significant effect of corrosion – it becomes rougher also some cavities and micro-cracks can be seen, Fig. 4(c). The roughness analysis of sample B gives the value R_a 20 nm and R_q 31 nm, Fig. 4(d). Many defects and craters appear, whose depth reaches values up to 160 nm, Fig. 4(c, d, e). The erosion degree of the coatings (sample C) becomes stronger after treatment at 500 °C and leads to deep cracks and formation of separate islands, Fig. 4(f). Duran *et al.* have proved that the SiO₂ coatings, deposited on stainless steel and galvanized steel, treated at 550 °C are more cracked because of the elimination of organic functional groups during the treatment, which reduces the plasticity of the coatings [43, 44].

The weight losses of the SiO₂ coatings (sample A) and the uncoated steel after 250 hours in the NaCl solution are 1.06 and 1.81 mg/cm², respectively. No weight changes are observed after 346 hours in corrosive environment,

Fig. 5. The weight losses of the SiO₂ coatings

Fig. 5. It can be seen that the sample A exhibits the better protection properties in comparison with the uncoated steel. The corrosion rate is evaluated according to the Standard ASTM G31. The corrosion rate of uncoated steel is 0.058 mm/year, while for samples A, B and C rates are 0.035; 0.092 and 0.133 mm/year, respectively.

The obtained results reveal that the SiO₂ coatings, obtained from 0.5M TEOS solution, exhibit the best protection properties. It is known that the microstructure and density of the SiO₂ films are highly dependent on the sol composition parameters, especially the concentration of silicon precursor. The concentration influences the density, surface topography (roughness), as well as some mechanical properties of the coatings: adhesion to the substrate, hardness, plasticity etc. It is known that after the coating deposition, there are large amounts of evaporated solvents and water, as well as organic residuals, which induce a substantial internal stress in the coatings [33]. This could be the reason for the formation of cracks. In the case of coatings B and C larger amounts of water and intermediates produced by hydrolysis are being probably evaporated during the process of decomposition of a highly concentrated TEOS solution. This process brings about formation of defects (pores, cracks and pits) on the surface, and also deteriorates the density and mechanical properties. Such combination between deteriorated surface characteristics and mechanical features (hardness, plasticity etc.) of these coatings seems to

be the reason for decreased corrosion resistivity. The silica coatings deposited from solution of lower Si concentration show enhanced protective performance, probably due to their improved surface and mechanical characteristics. The experiments concerning the dependence of mechanical properties on the sol-gel deposition parameters are still in progress.

3. MULTI-LAYER COATINGS FROM $\text{ZrO}_2/\text{SiO}_2$, $\text{TiO}_2/\text{SiO}_2$, $\text{CeO}_2/\text{SiO}_2$ AND $\text{Nd}_2\text{O}_3/\text{SiO}_2$ (According to the author's investigations)

3.1. Experimental part

ZrO_2 coatings have good chemical and thermal stability, high strength, high dielectric constant etc., which make them suitable for anticorrosion coating for steels protection [45]. TiO_2 coatings are also widely used as anticorrosion coatings on stainless steel [46–48]. The physical and chemical properties of both the ZrO_2 and TiO_2 films strongly depend on the deposition method and the corresponding heat treatment process [49]. Recently, multilayer coatings have been increasingly used as anticorrosive coatings because they provide better protective properties compared to monolayer coatings [50]. The multilayer configuration of the two types of oxides deposited to each other has the combined effect of their advantages, as a result thus prepared coatings should have increased corrosion resistance. The influence of the heating temperature on corrosion resistance of ZrO_2 and TiO_2 nano-sized coatings, deposited on silica under-layers, has been studied. The stainless steels are generally corrosion resistant that determines the significance of studies on the metal corrosion protection [51]. The sol-gel method is an environmentally friendly low-temperature technique for surface protection, which offers many advantages compared to the other methods due to the possibility of producing materials with controlled porosity, phase and chemical composition of the films deposited on different substrates [52]. The excellent chemical stability, good mechanical strength and enhanced corrosion resistance of the sol-gel protective oxide coatings make them suitable for various industrial applications and especially for the corrosion protection. Various protective inorganic oxide coatings such as SiO_2 , CeO_2 , ZrO_2 , etc. have been studied to enhance the corrosion resistance of the steels [53–55]. In view of previous experience in the corrosion investigation, it is well known that adding small amounts of dopants – for example rare earth elements (Ce, La etc.), greatly improves the corrosion resistance [56]. We have not found in the available literature information concerning the resistance of Nd_2O_3 doped SiO_2 films in the NaCl medium. EDX

analysis of TiO_2 , ZrO_2 and CeO_2 multilayers coatings deposited on SiO_2 are given in Table 1.

Table 1. EDX analysis of TiO_2 , ZrO_2 and CeO_2 multilayer coatings deposited on SiO_2

Before corrosion test	O at%	Al at%	Si at%	Cl at%	Cr at%	Mn at%	Fe at%	Ni at%	Zr at%	Ce at%	Ti at%
SZ5	21.60	–	8.70	–	13.68	0.90	48.20	4.84	2.63	–	–
SZ7	30.70	–	11.42	–	12.18	1.06	38.47	4.17	2.00	–	–
SC5	19.46	–	6.54	–	15.18	1.01	51.83	5.51	–	0.48	–
SC7	24.12	–	7.11	–	14.31	1.04	47.75	5.23	–	0.44	–
ST5	20.93	–	9.15	–	14.04	1.20	48.40	5.52	–	–	1.07
ST7	28.10	–	8.53	–	13.48	1.01	43.21	4.64	–	–	1.00
After corrosion test											
SZ5	37.61	0.48	6.76	0.29	11.36	0.85	37.33	3.70	1.64	–	–
SZ7	40.57		5.58	0.26	11.65	0.74	35.57	3.61	2.01	–	–
SC5	28.98	0.54	5.62		13.66	0.87	45.50	4.53	–	0.30	–
SC7	40.35		11.78		10.58	0.68	31.94	3.86	–	0.36	–

3.1.1. ZrO_2 multilayer thin films deposited on SiO_2 by dip coating

The stainless steel AISI 316 substrates with dimensions 7.5×2.5 cm pre-cleaned ultrasonically in ethanol and acetone are used. The solutions containing 0.5M Si are prepared from a TEOS in a mixture of ethanol, water and hydrochloric acid as a catalyst and stirred for 2 hours. The H_2O :TEOS molar ratio is 3.7. The solutions are subjected to aging 7 days in order to produce sols with desire viscosity. Metal substrates are dipped in the sol and withdrawn at a constant speed of 3 cm/min, and then dried alternately at 60°C , 90°C and 300°C . These steps are repeated 2 times [57, 58].

Then, three layers of ZrO_2 are deposited on the SiO_2 thin films. The ZrO_2 solutions are prepared as follows: $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (precursor) is dissolved in ethanol up to 0.4M concentration; 0.016M acetylacetone (as a complex agent) is added, as well a few drops of nitric acid to prevent fast hydrolysis. The silica coatings are dipped in the sol and withdrawn at a constant speed of 3 cm/min, and then dried at 300°C for 80 minutes. These steps are repeated 3 times. The final sintering temperature for samples CZ5 ($\text{SiO}_2/\text{ZrO}_2$) is 500°C , as

well as 1 hour soaking is realized. For the samples CZ7 ($\text{SiO}_2/\text{ZrO}_2$) thermal treatment finishes at 700°C and also 1 hour soaking.

3.1.2. CeO_2 multilayer thin films deposited on SiO_2 by dip coating

Two layers of silica are deposited by the technology described above. 0.4M sol of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ is prepared by dissolution in isopropanol (sol Ce). Three layers of CeO_2 are deposited on the SiO_2 thin films following the next procedure: (i) the silica substrates are dipped in sol Ce and withdrawn at constant rate of 3 cm/min, and after that dried at 300°C for 80 minutes; (ii) some of dried samples are finally heated at 500°C , soaking 1 hour. The samples thus obtained are denoted SC5 ($\text{SiO}_2/\text{CeO}_2$). The other samples are sintered at 700°C , soaking 1 hour – SC7 ($\text{SiO}_2/\text{CeO}_2$).

3.1.3. Multilayer coatings of TiO_2 deposited on SiO_2 by dip coating

Two layers of silica are deposited on the steel in accordance with the above mentioned technology; after that 3 layers of TiO_2 are deposited on SiO_2 thin films. Titanium isopropoxide $\text{Ti}(\text{OC}_3\text{H}_7)_4$ (TTIP) (98% purity) is chosen as a precursor. TTIP is dissolved in a mixture of ethanol (EtOH) and butanol (ButOH). The resulting sol is transparent and orange. The reaction of the formation of a complex is exothermic. After vigorous stirring of the sol at a room temperature a mixture of distilled water and ethanol is added. Hydrochloric acid is chosen as a catalyst. The molar ratio of components is $\text{TTIP}:\text{EtOH}:\text{ButOH}:\text{H}_2\text{O}:\text{HCl} = 1:19:1:1:0.03$. The silica coatings are dipped in the sol and withdrawn at a constant speed of 3 cm/min, and then dried at 300°C for 80 minutes. These steps are repeated 3 times. Dried samples are separated in two batches – the first one is finally sintered at 500°C and 1 hour soaking. The heating rate is $3^\circ\text{C}/\text{min}$. The samples thus prepared are denoted ST5 ($\text{SiO}_2/\text{TiO}_2$). The samples prepared according to above mentioned technology and final temperature treatment at 700°C , 1 hour soaking, are denoted ST7 ($\text{SiO}_2/\text{TiO}_2$).

3.1.4. Multilayer coatings of Nd_2O_3 deposited on SiO_2 by dip coating

The substrates for sol-gel coatings are low carbon content constructions steel USt 37-1 plates (DIN 17 100) with perlite-ferrite type of structure [59]. They are degreased in hot acetone for 5 min using ultrasonic bath, then they are dried at 60°C in furnace. Ethanolic solution of tetraethyl orthosilicate

(TEOS, 99.5%, Merck) is hydrolyzed with water-ethanol mixture at a molar ratio $\text{TEOS}:\text{H}_2\text{O} = 4.7$. Hydrochloric acid (37%) is used to catalyze the hydrolysis process. The obtained sol (A) is used for deposition of non-doped SiO_2 coatings. Sol B is prepared by dissolving of Nd_2O_3 in small quantity of HNO_3 , followed by dissolving it into deionized water in order to obtain final concentration of neodymium salt 0.01 mol/L. The Nd_2O_3 doped SiO_2 coatings are produced by using mixtures of sol A and sol B. The concentration of the metal dopant is calculated in such a way as to give 0.14 wt% and 0.28 wt% Nd_2O_3 with respect to SiO_2 amount. The substrates are coated by spin-on technique at a constant speed of 800 rpm for 20 s. The coatings are then dried at 100°C for 20 min. These steps are repeated 7 times to obtain desirable films thickness. The final thermal treatment step is carried out in temperature-programmable oven at 300°C . The temperature is increased at a constant rate of $3^\circ\text{C}/\text{min}$. After 1 hour soaking the samples are cooled naturally down to a room temperature. The surfaces of the so prepared samples are investigated by SEM JCSA 733 JEOL.

The investigated samples were exposed to the action of salty solution of 3.5% NaCl at 35°C in the course of 12 hours to study their chemical resistance.

3.2. Results and discussion

The samples ST5 and ST7 contain slightly crystallized anatase phase according to X-rays diffraction data, Fig. 6. A similar result is recorded by Sheng and co-authors for the sol-gel layers of titanium dioxide doped with SiO_2 . They prove that the intensity of the anatase peaks diminish with an increase in the concentration of silicon dioxide. The authors also reveal that the titanium dioxide layers are amorphous, particle size reduces, and the anti-corrosion capacity of 304 stainless steels in 3.5% NaCl in the dark increases along with the SiO_2 content. According to Cheng *et al.* the additional SiO_2 causes an anatase and amorphous phases to disappear decreasing the photo-electrochemical property of coated 304 stainless steels [60]. Another group of researchers has also shown that the introduction of SiO_2 into TiO_2 nanoparticles slows the crystallization of the anatase phase [42].

Figure 7 shows the morphology of multilayer coatings with different oxides deposited on silica. $\text{SiO}_2/\text{ZrO}_2$ coatings are relatively dense with the presence of nano-sized pores, which increase in size at heat treatment temperature of 700°C , Fig. 7(a, b). In $\text{SiO}_2/\text{CeO}_2$ coatings there are no cracks and pores, but nano-crystallites with different sizes on the surface of the layer are visible, Fig. 7(c, d). The $\text{SiO}_2/\text{TiO}_2$ coatings have a similar structure, with the surface nano-crystallites being larger and more numerous, Fig. 7(e, f). At higher

(a)

(b)

(c)

(d)

(e)

Fig. 6. XRD of freshly obtained coatings from $\text{TiO}_2/\text{SiO}_2$, $\text{CeO}_2/\text{SiO}_2$, and $\text{ZrO}_2/\text{SiO}_2$ treated at 500 and 700 °C: (a) CS5; (b) CS7; (c) SZ5; (d) SZ7; (e) ST7

Fig. 7. Morphology of sol-gel coatings from freshly obtained:
 (a) SZ5; (b) SZ7; (c) SC5; (d) SC7; (e) ST5; (f) ST7

Fig. 8. Morphology of sol-gel coatings after corrosion test:
(a) SZ5; (b) SZ7; (c) SC5; (d) SC7

temperatures, sintering processes take place, as a result the number and size of surface crystals increase, and this effect is enhanced at $\text{SiO}_2/\text{TiO}_2$ coatings.

In Figure 8 it can be seen that the multilayer coatings of CeO_2 deposited on SiO_2 after corrosion attack have a preserved surface, without craters and cracks, which proves their high corrosion stability, Fig. 8(a, b). In contrast, the surface of $\text{ZrO}_2/\text{SiO}_2$ coatings is much rougher with multiple craters and pits, and these corrosion effects are enhanced in samples treated at higher temperatures (SZ7). The coatings of TiO_2 deposited on SiO_2 increase their roughness after the corrosion test, but retain their characteristic granular structure, without showing the effects of corrosion such as cracks and other defects, Fig. 9. The structure of the coatings treated at 700°C is similar.

Fig. 9. Morphology of sol-gel coatings ST5 after corrosion test

Fig. 10. Weight loss of multilayer coatings SiO₂/CeO₂, SiO₂/ZrO₂, and SiO₂/TiO₂ after corrosion attack

TiO₂/SiO₂ and CeO₂/SiO₂ coatings treated at a lower temperature show higher corrosion resistance than that of the ZrO₂/SiO₂ samples, which is in accordance with the results of NaCl weight loss test, Fig. 10. The protective properties of both types of coatings decrease with increasing of the temperature. The better protective properties of TiO₂/SiO₂ heated at 500 °C may be due to their poor crystallization and relatively dense surface. In contrast, the other 2 types of coatings show not so good barrier properties, which is probably due to the increased crystallization and the type of surface morphology. The obtained new multilayer TiO₂/SiO₂ structures are promising to increase the corrosion resistance of steel.

Fig. 11. SEM photograph of SiO₂ fresh films doped with 0.28% Nd₂O₃

The surfaces of SiO₂ films doped with Nd₂O₃ are examined by using a SEM. Figure 11 shows SiO₂ films doped with 0.28 wt% Nd₂O₃ [59]. The surface of the film is relatively dense without any visible cracks. The SEM micrographs of the coatings after carrying out resistance test in NaCl are shown in Fig. 12. It can be seen that on the surface of non-doped SiO₂ numerous visible cracks appear and the film is detached in some places, Fig. 12(a). The Nd₂O₃ doped silica coatings exhibit restricted lower number of cracks having smaller size. The films are more strongly adhered to the steel substrate surface in comparison with the non-doped SiO₂ coatings, Fig. 12(b, c). On the basis of the above mentioned results it can be concluded that the Nd₂O₃ doped silica coatings are more resistant to the NaCl corrosive attack than the non-doped coatings, probably due to the corrosion inhibiting effect of Nd³⁺ ions in the SiO₂ coatings similar to that of cerium ions [61]. These preliminary results

about the chemical resistance of doped SiO_2 coatings are promising and they give us the reason to extend the scope of the experiments further involving electrochemical measurements for estimation of corrosion resistance.

Fig. 12. SEM photograph of SiO_2 films: (a) after chemical resistance test; (b) doped with 0.14% Nd_2O_3 after chemical resistance test; (c) doped with 0.28% Nd_2O_3 after chemical resistance test.

4. CONCLUSION

The resistance of SiO_2 coatings in corrosive environments decreases with increasing concentration of TEOS solution. The coatings deposited from 2M solution show several micro-cracks. The surface of the coatings prepared from 0.5M TEOS solution preserves their integrity, only some pittings are observable. The corrosion rate of SiO_2 coated steel (0.035 mm/year) is lower than uncoated steel. The erosion of coatings treated at 500 °C becomes stronger and even eruption in some areas appears after corrosion attack. Silica coatings deposited from solution with lower Si concentration show enhanced anti-corrosion properties, probably due to their improved surface and mechanical characteristics (adhesion, plasticity etc.). The observed influence of both parameters TEOS concentration and temperature of treatment can be used for the tuning of the protective properties of SiO_2 sol-gel coatings.

The ZrO_2 coatings on SiO_2 are rougher than $\text{SiO}_2/\text{TiO}_2$ and $\text{SiO}_2/\text{CeO}_2$ coatings. The $\text{SiO}_2/\text{ZrO}_2$ and $\text{SiO}_2/\text{CeO}_2$ are relatively smooth without any visible pores. The TiO_2 and CeO_2 coatings deposited on SiO_2 under-layer manifest the higher corrosion resistance than that of $\text{SiO}_2/\text{ZrO}_2$ samples, which has been proved by the weight loss test in NaCl medium and SEM pictures. The better protective properties of $\text{SiO}_2/\text{TiO}_2$ and $\text{SiO}_2/\text{CeO}_2$ could be attributed to their low degree of crystallinity and relatively dense surface. The obtained new multilayer structures of $\text{SiO}_2/\text{TiO}_2$ (CeO_2 , ZrO_2) are promising with the view to increase the corrosion resistance of the steel.

The scanning electron photographs of the doped films reveal smoother surface in comparison with the non-doped films after chemical resistance test in corrosive NaCl medium. It has been revealed that Nd₂O₃ doped silica coatings can provide a higher chemical resistance.

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