

CORROSION STABILITY IN SALT MEDIUM OF STAINLESS STEEL AND CARBON STEEL, USING DIFFERENT OXIDE SOL GEL COATINGS

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Abstract. Three types of oxide sol gel coatings: TiO_2 , CeO_2 and TiO_2/CeO_2 composite were deposited by sol gel method on stainless steel and carbon steel. The morphology was examined by means of Scanning electron microscopy (SEM). X-ray diffraction analyses (XRD) were applied to investigate the phase composition. The corrosion resistances of the coatings were studied by evaluation of the weight loss in NaCl medium for 1200 hours. The surface of the TiO_2 samples were relatively dense with a few surface nanocrystals and after tests does not shown any signs of corrosion. The composite TiO_2/CeO_2 samples possess deep cracks which evidently favor the attacks in corrosion medium. Ceria and titania coatings deposited on stainless steel have zero weight loss in corrosive medium. The TiO_2 coatings could also effective protect carbon steel, while the TiO_2/CeO_2 and CeO_2 coatings exhibited lower corrosion resistance.

Keywords: SOL-GEL, NANOSIZED FILMS, PROTECTIVE PROPERTIES, FILMS

1. Introduction

The family of stainless steels is widely used in various industries as well as in the biomedical sectors due to its tailorable barrier, mechanical, etc properties and biocompatibility [1]. However, in the presence of halide ions, corrosion proceeds in stainless steels [2]. Carbon steels are the most commonly used pipeline materials in petroleum industry, but they are prone to corrosion in environmental containing CO_2 [3]. In order to overcome this problem various oxide films (SiO_2 , ZrO_2 , Al_2O_3 and TiO_2) can be deposited on the metals to improve their barrier properties [4,5]. Among them titania and ceria coatings are the most widely used the barrier properties of the steels. Pinzon et al have successfully obtained thermally sprayed alumina-titania anticorrosion coatings on carbon steel/DIN 1.0065 USt37-1/ [6]. The preparation and properties of TiO_2 - CeO_2 coatings by the sol-gel dip-coating process, using cerium chloride and various titanium alkoxides, and the effect of catalysts were studied. Gelation time of the coating solution became longer with an increase in the molecular weight of titanium alkoxide. The transmittance, thickness, chromaticity and acidic durability of the coating films were measured as a function of aging time of the coating solution. The most transparent and acidic durable coating film was obtained by using a solution just before gelation. In the case of using a solution with a catalyst, the thickness became thinner with increasing pH of the coating solution [7]. Mixed CeO_2 - TiO_2 films with different Ce/Ti mole ratios were prepared following an alcohol based sol-gel route via the spin coating technique using mixed inorganic-organic [$CeCl_3 \cdot 7H_2O$ and $Ti(OPr)_4$] precursors. Ion storage capacity for films obtained from aged sols was studied. Enhanced titanium oxide content improved the insertion capacity of the corresponding films as was evident from inserted charge determined by multiple step chronoamperometric measurements [8]. The aim of this study is to investigate and compare the corrosion behavior of three oxide coatings (CeO_2 , TiO_2 and CeO_2 - TiO_2) deposited on stainless steel AISI 316 and carbon steel.

2. Experimental procedures

2.1. Deposition procedures

Two types of substrates were used for the deposition of anticorrosion coatings: stainless steel AISI 316 and carbon steel/DIN 1.0065 USt37-1/. The substrates were cleaned ultrasonically in hot ethanol and acetone, after that were dried in air at 100°C. Three types of samples were prepared: cerium

oxide, titanium dioxide and titanium-cerium composite oxide. Cerium nitrate ($Ce(NO_3)_3 \cdot 6H_2O$) dissolved in isopropanol was used as precursor solution. The substrates were immersed in the solution and holding for 10 seconds, after that withdrawn at a speed of 30 mm/min. Then, the samples are dried in air first at 100°C for 1 hour, after which the temperature rises to 300°C for 1 hour. After fifth dipping-drying cycles the samples were treated at 400°C and were denoted as C1 (on stainless steel) and C3 (on carbon steel/DIN 1.0065 USt37-1/). Titanium isopropoxide (TTIP) were used to obtain the TiO_2 deposition solution. Acetylacetone (AcAc) is used as a stabilizing agent. Titanium isopropoxide (TTIP); $Ti(OC_3H_7)_4$, 98% purity, (Acros) and AcAc are dissolved in 2-propanol. The resulting solution is transparent and orange in color, which is typical of the chelated complex formed. The complex formation reaction is exothermic. After vigorous stirring at room temperature, a mixed solution of distilled water and i-propanol was added dropwise to the above solution under continuous stirring. The molar ratio of components is TTIP: iPrOH: H_2O :AcAc=1:30:1:1. The resulting solution was denoted as 1. Then the deposition-drying procedures and final treatment followed the scheme described deposition of CeO_2 coatings. The samples were denoted as T1 (on stainless steel) and T3 (on carbon steel). For the composite coatings were used solution mixture of titanium and cerium precursors in atomic ratio 30/70. Then the deposition-drying procedures and final treatment followed the scheme described deposition of CeO_2 coatings. The corresponding samples were denoted as CT1 (on stainless steel) and CT3 (on carbon steel)

2.2 Analyses

The phase compositions of the samples were studied by X-ray diffraction (XRD) with $CuK\alpha$ -radiation (Philips PW 1050 apparatus). A scanning electron microscope (SEM) Philips 515 was used for morphology observations of the films.

2.3. Evaluation of the corrosion resistance of the coatings.

The corrosion resistance of the samples was evaluated weight loss method, using salty corrosive solution of 3.5% NaCl at 25°C (EN ISO10289/2006). The corrosion resistance of the investigated samples and uncoated stainless steel (reference sample). The temperature of the solution and the air temperature were controlled by calibrated thermometers. The mass weight loss was determined after 1200 hours of corrosion attack.

3. Results and discussion

From the XRD analyses of the both C and CT samples confirm the presence of pure cubic CeO_2 phase according to JCPDS card 43-1002 with polycrystalline nature. It has to be note that in the composite CT1 and CT3 coatings (i) no peaks corresponding to anatase phase were detected; (ii) peak broadening was observed in comparison to the pure ceria coatings (Fig. 1a,b). X-ray diffraction pattern of T1 and T3 coatings revealed pure anatase phase without any peaks of rutile or brookite phase. The average crystalline size of CeO_2 coatings is 7 nm, while the composite materials have lower crystalline size - 4 nm. This may be due to the formation of Ce-O-Ti bonds, which inhibited the crystallite growth of TiO_2 . The TiO_2 crystallite size was calculated from the highest intensity plane (101) and found to be around 13 nm.

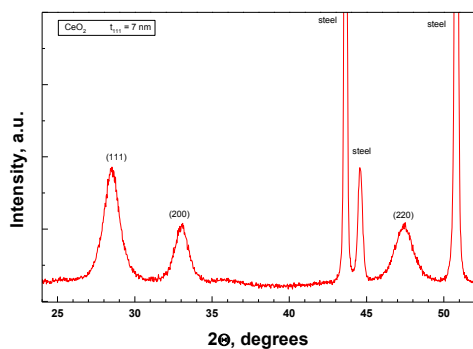


Fig. 1-a

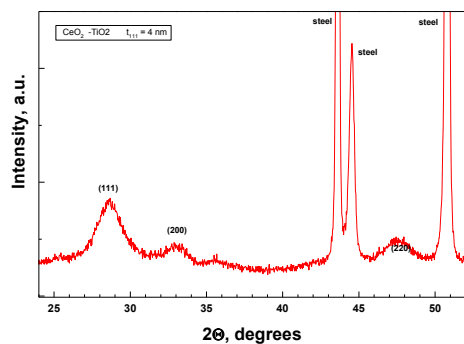


Fig. 1-b

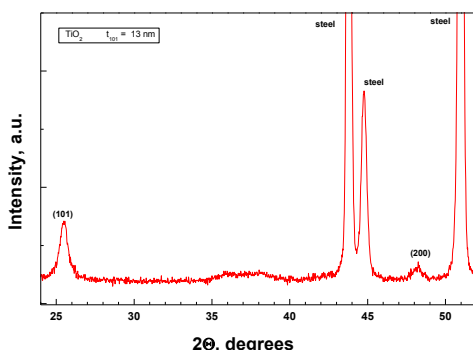


Fig. 1 - c

Fig. 1. XRD patterns of CeO_2 (a), $\text{CeO}_2\text{-TiO}_2$ (b) and TiO_2 (c) coatings on stainless steel AISI 316

Figure 2 shows the SEM images on the surface of the samples before and after the corrosion test. Sample C2 is relatively dense and smooth. After the corrosion test, the surface

retains its characteristics and holes, pits and other characteristic signs of corrosion are not observable (Fig 2b).

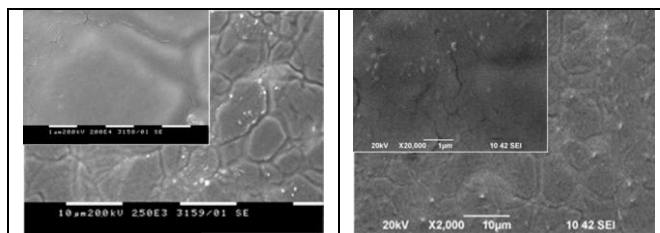


Fig. 2. Morphology of freshly prepared CeO_2 (C1) - (left) and after corrosion test (right)

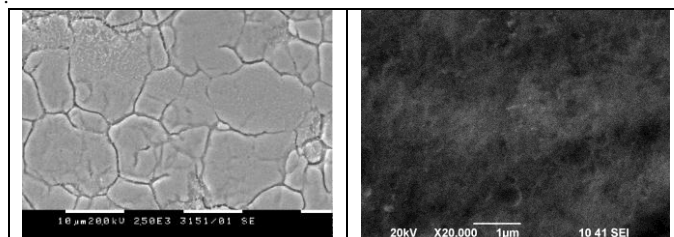


Fig. 3. Morphology of freshly prepared TiO_2 (T1) - (left) and after corrosion test (right) at higher magnification (20 000).

Fig. 3 shows the morphology of the TiO_2 coating, obtained from the titanium isopropoxide sol on stainless steel substrates. The surface is continuous, but microcracks are visible, which could be due to the small residual compressive stresses [9]. During the drying, crystallization and densification processes the coatings were subjected to fracture and macro cracking due to the intrinsic film stresses, caused by chemical reactions during drying, difference in thermal expansion coefficients between substrate and the TiO_2 film, grain interaction and grain size of the TiO_2 film [10]. Also the stainless steel substrate has a higher coefficient ($17 \times 10^{-6}/^\circ\text{C}$) of linear thermal expansion than the TiO_2 film ($2.1\text{--}2.8 \times 10^{-6}/^\circ\text{C}$) [11]. On cooling, the stainless steel substrate shrinks more than the TiO_2 film leading to the formation of small microcracks.

As can be seen the coating C3 has a relatively dense, but rough surface with several microcracks. After the corrosion attack the morphology changes, and visible signs of corrosion are visible (Fig 4-c,d).

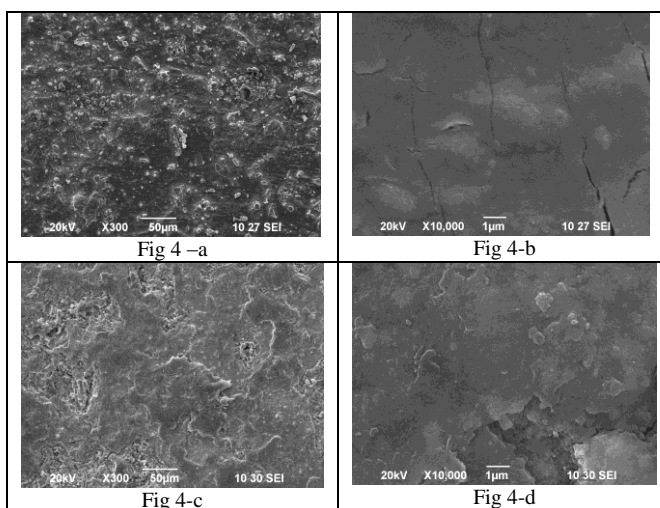


Fig. 4. Morphology of freshly prepared CeO_2 on carbon steel/DIN 1.0065 USt37-1/(C3) - (a,b) and after corrosion test (c,d).

It has to be note that the surface morphology of TiO_2 coating is a relatively dense without cracks. (Fig. 5) It is obvious numerous small crystallites on the surface. After the immersion in corrosive salt medium the surface of titania coating remains almost unchanged even

such long period of time. This result proves the good barrier properties of TiO_2 coatings deposited on carbon steel/DIN 1.0065 USt37-1/.

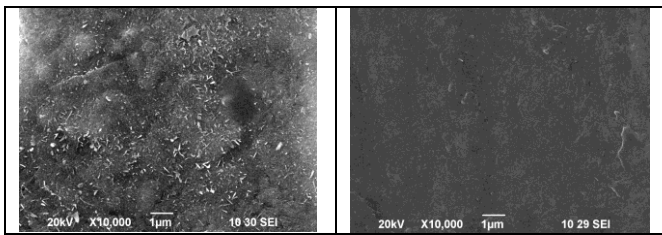


Fig. 5. Morphology of freshly prepared TiO_2 coatings on carbon steel/DIN 1.0065 USt37-1/ (T3) - (left) and after corrosion test (right).

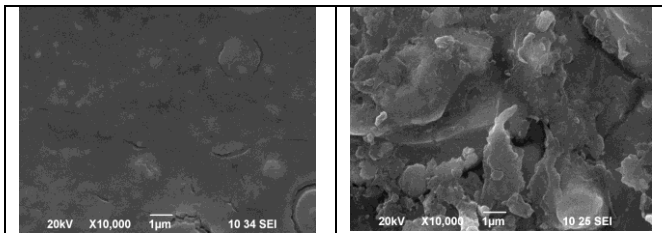


Fig. 6. Morphology of freshly prepared CeO_2 - TiO_2 coatings on carbon steel/DIN 1.0065 USt37-1/ (CT3) - (left) and after corrosion test (right).

It has to note that the corrosion attack influences significantly the surface features of the composite CT coatings. The SEM pictures revealed deep craters and even sections, where the coating has begun to be removed from the substrate.

Table 1. Corrosion rate for all tested coatings after 50 and 1200 hours corrosion attack.

Sample Code	K_{50} [g/m ² h]	K_{1200} [g/m ² h]
CT 1	0	0.002
CT3	0.030	0.028
C 1	0	0
C 3	0.021	0.032
T 1	0	0
T3	0.002	0.007

The analysis of the results of the corrosive test is as follows. For CT samples the corrosion rate K is the lowest for CT1 (after the first fifty hours it is zero) and the highest for CT3. In the Ce series in the Ce1 sample there is no corrosion process during the first fifty hours, and in the second run (1200 hours) the weight loss is negligible and the value of K is equal to zero. These results refer to both test periods. In the TiO_2 coatings, T1 corrosion rates K are zero for both test periods due to minor weight changes. In T3, the corrosion rate is higher than that of T1 in both periods.

The weight loss of CT coatings deposited on stainless steel after corrosion attack is 7×10^{-5} g/m², while for T1 and C1 zero weight loss was observed (Fig. 7) The corrosion resistance of the all investigated coatings on stainless steel is higher, than those on carbon steel/DIN 1.0065 USt37-1/. The results presented on Figures 6 and 7 confirm that TiO_2 coatings exhibit increased ability to protect both the stainless and carbon steels, in comparison to that of C and CT coatings. This result probably is due to the less pronounced crystallization of titanium dioxide (Fig. 1-c) and suitable surface features.

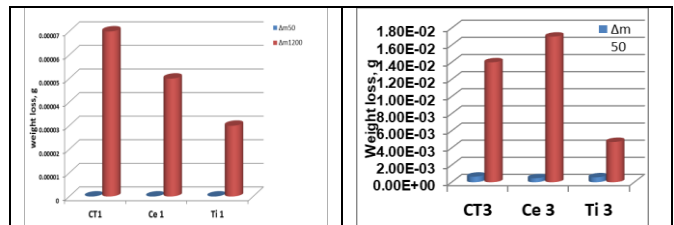


Fig. 7. Weight loss for all tested coatings after 50 and 1200 hours corrosion attack.

4. Conclusion

The anticorrosion resistance of stainless steel and carbon steel coated with several coatings: TiO_2 , CeO_2 and $\text{TiO}_2/\text{CeO}_2$ by sol gel method were investigated. The coatings on stainless steel are relatively dense. After the corrosion attack the morphology of cerium dioxide coatings changes, and visible signs of corrosion are visible. It is obvious numerous small crystallites on the surface. The composite $\text{TiO}_2/\text{CeO}_2$ samples possess deep cracks which evidently favor the attacks in corrosion medium. Titania coatings exhibit good barrier properties both on stainless steel and carbon steel: the surface of titania coating remains almost unchanged even at such long period of corrosion attack. Ceria and titania coatings deposited on stainless steel have zero weight loss in corrosive medium. The TiO_2 coatings could also effectively protect carbon steel, while the $\text{TiO}_2/\text{CeO}_2$ and CeO_2 coatings exhibited lower corrosion resistance. This results could be due to the less pronounced crystallization and suitable surface morphology of the titania coatings.

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5. Literature

- [1] Fini M, Aldini N. N, Torricelli P., Giavaresi G., Borsari V., Lenger, H, Bernauer J., Giardino R., Chiesa R, Cigada A., Biomaterials 24 (2003) 4929.
- [2] Durán A., Castro Y., Aparicio M., Conde A., De Damborenea J.J., Protection and surface modification of metals with sol-gel coatings, Intern.Mater.Rev. 52 (2007) 175.
- [3] Lopez D.A., Simison S.N., Sanchez SR., The influence of steel microstructure on CO_2 corrosion. EIS studies on the inhibition efficiency of benzimidazole, Electrochim. Acta, 48 (2003) 845-85
- [4] Padhy N., Mudali U.K, Chawla V., Chandra R, B. Raj, Mater. Chem. Phys. 130 (2011) 962.
- [5] Gallardo J., Duran A., Damborenea J.J., Corros. Sci. 46 (2004) 795.
- [6]. Pinzón A. V., K. J. Urrego, A. González-Hernández, M. R Ortiz, F.V. Galvis, Corrosion protection of carbon steel by alumina-titania ceramic coatings used for industrial applications, Ceram. Intern., 44 (2018), 21765.
- [7]. Makishima, A., Asami M., Wada K, Preparation and properties of TiO_2 - CeO_2 coatings by the sol-gel process, J. Non-Crystall. Solids, 121(1990)310.
- [8]. Makishima, A., Asami M., Wada K., Preparation and properties of TiO_2 - CeO_2 coatings by the sol-gel process, Journal of Non-Crystalline Solids, 100 (1988) 321.
- [9]. Exarno, G. J., Hess N. J, Spectroscopic measurements of stress relaxation during thermally induced crystallization of amorphous titania films, Thin Solid Films 220 (1992) 254.
- [10]. Teeuw D. H. J., De Haas M., De Hosson J. Th. M, Residual stress fields in sol-gel-derived thin TiO_2 layers, J. Mater. Res. 14 (1999) 1896.
- [11]. Scott, M. L., Nat. Bur. Stand. (US) Spec. Publ. 688 (1985) 329.