Enhancement of corrosion resistance of steel, coated with various coatings on the base of SiO_2, TiO_2, ZrO_2 and CeO_2

Stancho Yordanov[1,*], Irina Stambolova[2], Lyuben Lakov[1], Mihaela Aleksandrova[1], Bojidar Jivov[1], Vladimir Blaskov[1], Nikolai Boshkov[3],

[1]Bulgarian Academy of Sciences, Institute of Metal Science, Equipment and Technologies with Hydro and Aerodynamics Centre "Acad. A. Balevski", , e-mail: stancho14@abv.bg.
[2]Bulgarian Academy of Sciences, Institute of General and Inorganic Chemistry,
[3]Bulgarian Academy of Sciences, Institute of Physical Chemistry "Rostislaw Kaishev,

Abstract: *Different corrosion-resistant coatings based on various SiO_2, TiO_2, ZrO_2 and CeO_2oxides have been applied to various steels by the sol-gel method and spray pyrolysis. The obtained experimental coatings were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM) and weight loss measurements in 3.5% NaCl medium. TiO_2 / SiO_2 and CeO_2/SiO_2 coatings treated at lower temperatures (500oC) have been shown to exhibit higher corrosion resistance than ZrO_2/SiO_2 samples. Increasing the treatment temperature decreases the protective properties of the invesitgated coatings. The enhanced protective properties of TiO_2/SiO_2 are probably due to their low crystallized fine grained structure and relatively dense surface without visible cracks.*
Keywords: *SOL-GEL SPRAY PYROLYSIS, CORROSION RESISTANT COATINGS*

1. Introduction

The high hardness, corrosion stability, high temperature strength and oxidation resistance make stainless steel an ideal material ,but unfortunately, in the presence of aggressive environments (for instance halide ions) proceeds excessive corrosion attack on the steels surfaces. [1] Corrosion of the marine equipments (i.e crude oil tankers, oil platforms and gas extraction) is very serious problem, because in salt water, which is a conductor of electricity, the potential difference between adjacent metals cause electrons to flown from one metal to the other, causing galvanic corrosion. The eventual corrosion destruction of shipping facilities could lead to spills and other environmental disasters, damaging ecosystems and environmental pollution, which not only results in material losses, but it is dangerous for human life. Inorganic substances especially arsenic and chromium salts are often used to prevent steel corrosion, but they are highly toxic for human health and environment and have to be replaced. Many other strategies are applied - one of most effective is the deposition of non-toxic oxides coating as barrier layers, such as CeO_2, ZrO_2, TiO_2, hybrid coatings etc. [2]. The effect of the change of various technological parameters such as the type of precursor, heat treatment, introduction of various dopants, etc. are investigated on the crystalline structure, the density and hydrophobicity of the coatings and hence their corrosion protective properties. Several types of mono component and bicomponent oxide coatings have been synthesized using the sol gel method. The aim of this study is to obtain corrosion resistant coatings of various inorganic oxides (pure and composite) TiO_2, CeO_2 and ZrO_2 deposited on SiO_2 by sol gel method . The selected sol gel method have advantages such as low cost of equipment, the ability to apply larger size pads that give potential for industrial application[3].

2. Experimental

AISI 316 stainless steel, 7.5x 2.5 cm in size, was ultrasonically cleaned in ethanol and acetone as substrates. The SiO_2 layers were applied from a solution of tetraethoxysilane (TEOS) in a mixture of ethanol, water and hydrochloric acid as a catalyst and stirred for 2 hours to form a 0.5M solution. The molar ratio of H_2O: TEOS is 3.7. The solution is aged for 7 days to form bonds in them. The metal pads are immersed in the solution and drawn at a constant speed of 3 cm / min and then dried successively at 60°C and at 90°C and 300°C. These steps are repeated 2 times.

The coatings are characterized by a set of physicochemical methods such as X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray photoelectric spectroscopy (XPS), energy dispersive analysis (DDA) analysis, EDA), infrared spectroscopy (IR), and more.

Corrosion resistance was assessed by two techniques: weight analysis after residence in NaCl salt fog.

3. Results and Discussion

Multilayer coatings of ZrO_2/SiO_2, TiO_2/SiO_2 and CeO_2/SiO_2 incl.

3.1 Multilayer coatings of ZrO_2 deposited on SiO_2 support by sol-gel method with immersion technique.

3.2 Multilayer coatings of CeO_2 deposited on SiO_2 by sol-gel method with immersion technique.

3.3 Multilayer coatings of TiO_2 deposited on SiO_2 support by sol-gel method with immersion technique.

In connection with 3.1, three layers of ZrO2 from the solution obtained as follows are applied to the specimens. $ZrOCl_2.8H_2O$ dissolved in ethanol to 0.4M solution was used as a precursor. 0.016 mol of acetylacetone is added as a complexing agent of droplets and a few drops of nitric acid to prevent hydrolysis. Substitutes of silica deposited are immersed in the solution and drawn at a constant speed of 3 cm/min and then dried successively at 300°C for 80 min. at a heating rate of 3°C/min for some of the specimens, while for others the above technology is repeated as the final heat treatment is carried out at 700°C for 1 hour in air.

Initially, 2 layers of silicon dioxide were applied in accordance with 3.2 using the above-described technology, after which 3 layers of CeO_2 were applied. $Ce(NO_3)_3.6H_2O$ dissolved in isopropanol to 0.4M solution was used as a precursor. Substitutes of silica deposited were immersed in the solution and withdrawn at a constant speed of 3 cm / min and then sequentially dried at 300°C for 80 min. These steps were repeated 3 times, finally finishing at 500°C for 1 hour in air at a heating rate of 3°C/min.

The initial 2 layers of silica were applied in accordance with 3.3 according to the above technology, after which 3 layers of TiO2 were applied and titanium isopropoxide (TTIP) was used as a precursor; Ti $(OC3H7)_4$ (98% purity) which was dissolved in a mixture of ethanol (EtOH) and butanol (ButOH). The reaction of complex formation is exothermic. After vigorous stirring at room temperature, a mixed solution of distilled water and ethanol was added drop wise to the above solution with stirring. Hydrochloric acid is added drop wise as a catalyst. The molar ratio of the components is TTIP: EtOH: ButOH: H_2O: HCl = 1: 19: 1: 1: 0.03. The silicon-coated substrates were immersed in the solution and drawn at a constant speed of 3 cm / min and then dried successively at 300°C for 80 min. These steps were repeated 3 times, finally finishing at 500°C for 1 hour air with a heating rate of 3°C / min, while in others the above technology is repeated, with the final heat treatment being carried out at 700°C for 1 hour of air.

The XRD of samples slightly crystallized the anatase TiO_2 phase. A similar result was reported by Cheng and co-authors for sol-gel layers of titanium dioxide doped with SiO_2. They demonstrate that the anatase phase peaks attenuate with increasing silicon dioxide concentration, as for the doped with 0% SiO_2 the titanium dioxide layer is amorphous [4] Another group of researchers also showed that the introduction of SiO_2 into TiO_2

nanoparticles slows the crystallization of the anatase phase. Figures 1 and 2 show the results of the XRD performed on the obtained experimental coatings.

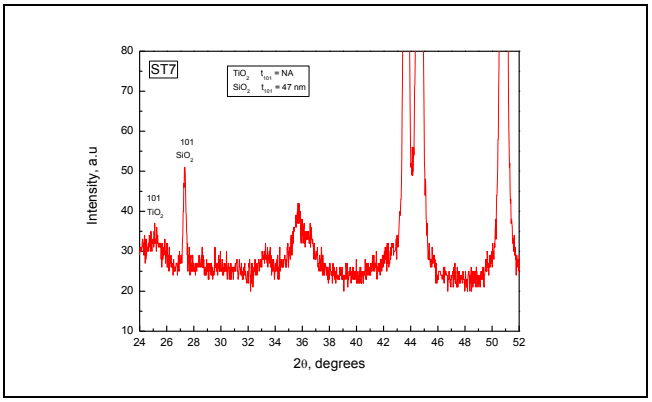

Fig. 1. *XRD of the TiO_2 deposited on SiO_2 coatings*

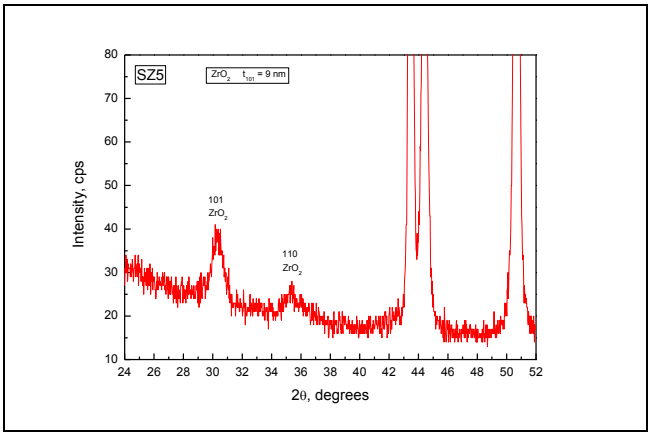

Fig. 2. *XRD of the ZrO_2 deposited on SiO_2 coatings.*

Legend:

SC5 -CeO_2 on SiO_2, treated at 500°C
SC7 -CeO_2 on SiO_2, treated at 700°C
ST5 -TiO_2 on SiO_2, treated at 500°C
ST7 -TiO_2 on SiO_2, treated at 700°C
SZ5 -ZrO_2 on SiO_2, treated at 500°C
SZ7 -ZrO_2 on SiO_2, treated at 700°C

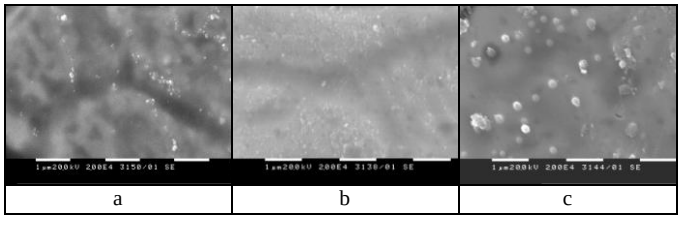

Fig 3. *Morphology of coatings – SZ5 (a), SC5(b) and ST5(c).*

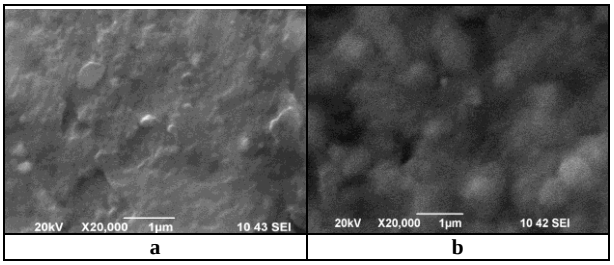

Fig 4. *Morphology of coatings – SC5 (a) and ST5(b) after corrosion test.*

Figures 3 and 4 show the morphology of coatings. The multilayer coatings of CeO_2/SiO_2 after corrosion attack have a preserved surface, without craters and cracks, which proves their high corrosion stability (Fig. 4 a). In contrast, the surface of ZrO_2/SiO_2 coatings is much more rough with many craters and pits, and these corrosion effects are exacerbated by samples treated at higher temperature (SZ7) (not shown). TiO_2/SiO_2 coatings after the corrosion test slightly increase their roughness but retain their characteristic grain structure, without exhibiting corrosion effects such as cracks, pores and other defects (Fig. 4b).

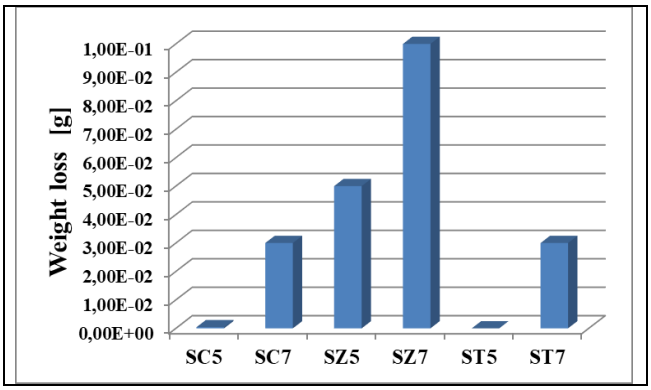

Fig. 5. *Weight loss of SiO_2/CeO_2, SiO_2/ZrO_2, and SiO_2 /TiO_2 multilayer coatings after corrosion attack..*

TiO_2/SiO_2 and CeO_2/SiO_2 coatings treated at a lower temperature exhibit higher corrosion resistance than ZrO_2/SiO_2 samples (Fig.5), as evidenced by the weight loss test in NaCl medium and the studies of morphology. Increasing the processing temperature impairs the protective properties of the two types of coatings. The better protective properties of TiO_2/SiO_2 heated at 500°C may be due to their very weak crystalline structure and relatively dense surface. In contrast, the other 2 types of coatings exhibit weaker barrier properties, which is probably due to the increased crystallization and the type of surface morphology.

The new TiO_2/SiO_2 multilayer structures obtained are promising with a view to increasing the corrosion resistance of the steel.

4. Conclusions

It was proved that TiO_2/SiO_2 and CeO_2/SiO_2 coatings treated at a lower temperature exhibit higher corrosion resistance than ZrO_2/SiO_2 samples, as evidenced by the NaCl medium weight loss test and morphology studies. It has been found that decreased treatment temperature (up to 500°C) enhances the protective properties of the two types of coatings. The better protective properties of TiO_2/SiO_2 treated at 500°C are due to their lower degree of crystallinity and relatively dense surface. In contrast, the other two types of coatings exhibit slightly lower barrier properties.

The new TiO_2/SiO_2 multilayer structures obtained are promising approach for increasing the corrosion resistance of the steel.

5. References

[1] D. H. Abdeen, M. El Hachach, Mr Koc, M. A. Atieh, Materials 2019, 12, 210
[2] Ohko Y, Saitoh Sh, Tatsuma T and Fujishima A 2001 *Journal of the Electrochemical Society* **148** B24].
[3] D. Wang, G.. P. Bierwagen, Progress in Organic Coatings 64 (2009) 327–338
[4] W.Cheng, Ch. Li. X Ma, L Yu, G. Liu, Mater. & Design 126 (2017) 155
[5] Bo-H. Kim, S K. Nataraj, K. S. Yang, H.-G. Woo, J Nanosci. Nanotechnol. 10 (2010) 3331.