Anticorrosion Sol-Gel Coatings of CeO$_2$, ZrO$_2$ and TiO$_2$
Deposited on SiO$_2$ Underlayer

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Abstract
Three types of oxide coatings: titanium dioxide, zirconium dioxide and cerium dioxide were deposited on SiO$_2$ underlayers by sol-gel method. The morphology was investigated by means of scanning electron microscopy (SEM) and the phase composition detected by X-ray diffraction analyses. The corrosion resistances of the coatings were examined in NaCl medium. The SiO$_2$/TiO$_2$ and SiO$_2$/CeO$_2$ coatings possess relatively smooth surface with some crystallites on the surface. The ZrO$_2$ coatings on SiO$_2$ are not smooth. According to the results of corrosion test the SiO$_2$/TiO$_2$ coatings exhibit the highest corrosion resistance. The most susceptible to the corrosion attack are the ZrO$_2$/SiO$_2$ coatings. After corrosion test the surface of these coatings became rougher with many pits. The better protective properties of SiO$_2$/TiO$_2$ and SiO$_2$/CeO$_2$ could be attributed to their low degree of crystallinity and relatively dense fine grain surface.

Keywords: sol-gel, multilayers, nanosized films, barrier properties,

1. Introduction

The stainless steels are generally corrosion resistant, but the composition of operating environment limits their chemical stability [7]. This consideration determines the significance of studies on the metal corrosion protection.

The sol–gel method is an environmentally friendly low temperature technique of 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 on different substrates [2]. The excellent chemical stability, good mechanical strength and enhanced corrosion resistance of the sol–gel protective ceramic 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 for enhancement of the corrosion resistance of the steels [3-5].

The purpose of this study was to investigate the enhancement of corrosion resistance of stainless steel substrate with multi-coatings, which consist of SiO$_2$ as under-layer and upper layers of ZrO$_2$, CeO$_2$ or TiO$_2$. 
2. Experimental

2.1 Preparation

Stainless steel samples AISI 316 7.5x 2.5 cm were cleaned ultrasonically in ethanol and acetone. The SiO2 under-layers were applied from a solution of tetraethyloxysilane (TEOS) in a mixture of ethanol, water and hydrochloric acid as a catalyst. The molar ratio H2O: TEOS is 3.7. The solution undergoes aging for 7 days. The metal substrates are immersed into the solution and withdrawn at a constant rate of 3 cm / min and then dried at 60°C and at 90°C and finally treated at 300°C. These steps are repeated two times. For SiO2/ZrO2 (SZ) samples on SiO2 under-layers 3 layers were deposited using ZrOCl2.8H2O and acetylace tone and then dried sequentially at 300°C. These steps are repeated 3 times, ending finally with calcination at 500°C. The same procedure was applied for the preparation of SiO2/CeO2 (SC) and SiO2/TiO2 (ST) samples. The CeO2 films were obtained from Ce(NO3)3.6H2O ethanolic solution, while the TiO2 coatings were deposited with precursor titanium tetraisopropoxide (TTIP); Ti(OC3H7)4 (98%), dissolved in a mixture of ethanol (EtOH) and butanol (ButOH).

2.2 Characterization

The phase compositions of the samples were studied by X-ray diffraction (XRD) with CuKa-radiation (Philips PW 1050 apparatus). A scanning electron microscope (SEM) Philips 515 was used for morphology observations of the films. The chemical corrosion resistances of the investigated samples and uncoated stainless steel (reference sample) were studied using salty corrosive aqueous solution of 3.5% NaCl at 25°C (EN ISO10289/2006. The temperature of solution and the air temperature were controlled by calibrated thermometers. The mass weight loss was determined after 200 hours of corrosion attack.

3. Results and discussion

The Figure 1 indicates the presence of ZrO2 and SiO2 crystallographic phases in sample SZ. The XRD data for sample SC shows that during the isothermal heating both phases are formed: nanocrystalline phase cubic CeO2 phase /diffraction file PDF 43-1002/ and SiO2 phase. The X-ray diffraction patterns of sample ST do not indicate the presence of a crystalline phase of TiO2, so the sample has amorphous structure (Fig. 3). The same result was obtained by Cheng and co-authors for sol-gel SiO2 doped titanium dioxide films [6]. They have proved that the peaks intensity of the anatase phase is weakening with an increase in silica concentration and the films doped with 20% SiO2 is amorphous. Another group of researchers also showed that the introducing of SiO2 into TiO2 nanoparticles suppress the crystallization of the anatase phase [7]. It should be pointed out that ZrO2 coating in SZ sample displays much larger crystallites sizes (44 nm) than those of CeO2 in SC coatings (6 nm).
Fig. 1 XRD pattern of SiO$_2$/ZrO$_2$ sample.

Fig 2 XRD pattern of SiO$_2$/CeO$_2$ sample.

Fig. 3 XRD pattern of SiO$_2$/TiO$_2$ sample
Fig. 4 shows the surface of the substrates before (a) and after 346 hours of corrosion test. (b) It is clearly visible, what are the surface changes of the steel after corrosion test - larger craters and holes (0.1-0.5 microns).

![Fig. 4. SEM photographs of stainless steel surface before (a) and after corrosive attack](image)

Figure 5 shows the morphology of multi-layered freshly prepared ZrO$_2$, CeO$_2$ and TiO$_2$ coatings on silicon dioxide and also after the corrosion test. Coatings SiO$_2$/ZrO$_2$ are relatively thick with the presence of nanosized pores (Fig 5a). In the SC sample surface nanocrystals of different sizes are observable on the surface. There are no visible cracks and pores (Figure 5b). A similar structure with larger and more numerous superficial nanocrystals is shown by SiO$_2$/TiO$_2$ coatings (Fig. 5c). From the Figure 5 it can be seen that the SiO$_2$/ZrO$_2$ coatings are rougher with a numerous craters and pits (Figure 5d). In contrast to it, the surface of CeO$_2$ coatings, deposited on silica under-layer after the corrosion attack is almost unchanged without any craters and cracks, which proves the high corrosion stability of the multilayer (Figure 5e). After corrosive attack the roughness of titania coatings deposited on SiO$_2$ increases slightly without showing any effects of corrosion such as cracks and other defects. (Figure 5f).

![Fig. 5 SEM photographs of freshly prepared SZ (a), SC (b) and ST (c) samples and after corrosion test SZ (d), SC (e) and ST (f)](image)

Initially, the structure and behaviour of steel 316 as a reference sample was investigated in a 3.5% NaCl corrosion environment. The weight loss after 250 hours in the NaCl solution was 18.1 g/m$^2$. 

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As it can be seen in the Figure 7 the investigated three types of multilayers exhibit improved corrosion resistance in comparison with those of the uncoated stainless steel. The best barrier properties were shown by the multilayers, which consist of SiO₂ underlayers, heated at 300°C and TiO₂ heated at 500°C. The SiO₂/TiO₂ coatings zero weight loss was registered after 200 hours of corrosion test. The possible reason for this behaviour is the low degree of crystallinity of the titania coatings, which improves their anti-corrosion properties. According to the authors in ref. [8] the presence of amorphous structure of TiO₂–CeO₂ composite deteriorates the ion and electron conduction of the films, which in its turn improves the barrier properties. The samples SiO₂/CeO₂ showed higher corrosion resistance than those of the SZ multilayer, which could be due to the lower degree of crystallinity and fine grain dense structure.

4. Conclusions

Multilayers on the basis of SiO₂/ZrO₂, SiO₂/CeO₂ and SiO₂/TiO₂ were obtained by sol – gel technology. The ZrO₂ coatings on SiO₂ are rougher than SiO₂/TiO₂ and SiO₂/CeO₂ coatings. The SiO₂/ZrO₂ and SiO₂/CeO₂ are relatively smooth without any visible pores. The TiO₂ and CeO₂ coatings deposited on SiO₂ under-layer manifested the higher corrosion resistance than that of SiO₂/ZrO₂ samples, which have been proved from the weight loss test in NaCl medium and SEM pictures. The better protective properties of SiO₂/TiO₂ and SiO₂/CeO₂ could be attributed to their low degree of crystallinity and relatively dense surface. The obtained new multilayer structures of SiO₂/TiO₂ (CeO₂, ZrO₂) are promising with the view to increase the corrosion resistance of the steel and this fact gives us the reason to extend the scope of the experiments.

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References