DEVELOPMENT OF NEW NANOSIZED SOL GEL COATINGS ON STEEL WITH ENHANCED CORROSION RESISTANCE

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***Abstract**: Sol gel method is a simple a low cost technique, which gives possibility to deposit coatings with definitely chemical and phase composition at low temperatures. Here we report an application of sol gel method by dip coating technique to prepare a several type of nanosized coatings: (a) one-component coatings such as TiO_2 and Nd doped TiO_2 (b) two types of bi-component layers, which contain as underlayer SiO_2 and upper layer TiO_2 or CeO_2. The coatings were characterized by XRD, SEM and AFM analyses. The XRD data revealed anatase phase for TiO_2 and Nd doped TiO_2 coatings. The presence of cubic CeO_2 and SiO_2 crystallographic phases were proved in SiO_2/CeO_2 sample. The morphological investigations of the coatings revealed that they have relatively dense surface. The anticorrosion properties were estimated by exposing the samples to the action of salty solution of 3.5% NaCl and was evaluated by their weight losses. Corrosion attack induces insignificant alteration of the surface morphology of both Nd doped TiO_2 samples and multilayer barrier coatings. Pits and other significant visible signs of corrosion are not found according to AFM and SEM analyses. The results proved that the investigated bi-component oxide coatings on the base of titania and ceria deposited on SiO_2 exhibit better corrosion resistance than the non-coated steel and one component samples. These type of oxide coatings could be perspective for various applications in industry due to their good anticorrosion properties.*

Keywords: Sol gel method, nanomaterials, nanosized coatings

1. Introduction

It is well know that the majority of metals and alloys even stainless steel are susceptible to corrosion attack in medium which contains halide ions. In order to overcome this problem, several barrier oxide coatings could be deposited on the metals. Among them, the most widely studied are CeO_2, TiO_2, ZrO_2, SiO_2 etc [1-3] The method for deposition of these coatings could be physical or chemical. Contrary to the physical deposition methods, the sol-gel method has the advantages of high chemical homogeneity, low cost, effectiveness and feasibility for mass production. During the last years a new approach is applied- deposition of coatings composed by 2 or 3 types of oxides, which deposited over the other. The new multilayer materials blend the advantages of the individual component oxides. It was proved by Alat et al. that the multicomponent coatings exhibit higher anticorrosion resistance than one component. [4]. The aim of this study is to compare the corrosion properties of one-component TiO_2 coatings and bi-component CeO_2 or TiO_2 coatings, on silica sol gel underlayer, which are prepared by dip coating technique.

2. Prerequisites and means for solving the problem

The stainless steel are widely used in all world infrastructures, but due to the electrochemical reactions in the environment the corrosion process of steels proceeds spontaneously and can not measure or control it. In this The efforts of researchers is to provide more effective corrosion protection of steel. This can be overcome by using of protective inorganic layers deposited on the steel. There are several methods of corrosion control: inhibitors, cathodic protection and applying of protective organic or inorganic coatings. The ceramic nanosized oxide coatings are potential good candidates due their excellent chemical stability.

3. Solution of the examined problem

Taking into account the excellent pysicochemical properties of CeO_2 and TiO_2 (chemical stability, high corrosion resistance, thermal and mechanical properties etc.), we have chosen these oxides in order to apply them as protectrive films against corrosion. As the bi-component coatings combines the advantages of the both constituents we have examined and compare the barrier properties against the corrosion of one component TiO_2 coatings and bicomponent CeO_2 or TiO_2 coatings, deposited over silica sol gel underlayer.

3.1. Experimental procedure for one component oxide coatings

Titanium isopropoxide (TTIP); $Ti(OC_3H_7)_4$, 98% purity, (Acros) and AcAc were dissolved in 2-propanol under vigorous stirring. (sol A) The molar ratio of components is TTIP: iPrOH: H_2O: AcAc = 1: 30: 1: 1. The resulting sample was denoted as TP. For doped TiO_2 coatings, definite quantity of Nd_2O_3 was dissolved in 2 ml of nitric acid and isopropanol and was added to sol A to obtain TiO_2 doped with 1at% Nd. (Sample TP-1). After cleaning the steel subtrates in acetone, they were dipped into each of the precursor solutions and held for 10 seconds, then withdrawn (velocity 30 mm/min). After each deposition, the samples were air-dried in two stages: first at 100°C, after which the temperature is raised to 300°C for 1 hour. These procedures (dipping-drying) were repeated and then the deposits were treated at 500° C for 1 hour.

3.2. Experimental procedure for bi-component oxide coatings

The SiO_2 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 H_2O: 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^{o}C. These steps are repeated two times. For SiO_2/CeO_2 (SC) samples on SiO_2 under-layers 3 CeO_2 layers were deposited using $Ce(NO_3)_3.6H_2O$ ethanolic solution, then was 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 SiO_2/TiO_2 (ST) samples, using as precursor titanium tetraisopropoxide (TTIP); Ti $(OC_3H_7)_4$.

3.3. Characterization

The phase compositions of the samples were studied by X-ray diffraction (XRD) with CuKα-radiation (Philips PW 1050 apparatus).The surface topography was studied by means of Atomic Force microscope (AFM) (NanoScopeV system, Bruker Inc.) operating in tapping mode in air. The scanning rate was set at 1 Hz. Subsequently, all the images were flattened by means of the Nanoscope software. The AFM images are calculated. The roughness analysis gives the value R_a, which is an arithmetic average of the absolute values Zj of the surface height deviations measured from the mean plane, while the image R_q is the root mean square average of height deviations taken from the mean image data plane. A scanning electron microscope (SEM) Philips 515 was used for morphology observations of the films.

3.4. Corrosion test

The chemical corrosion resistance of the investigated samples and uncoated stainless steel (reference sample) were studied using salty corrosive 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 estimated after 200 hours of corrosion attack.

4. Results and discussion

X-ray diffraction analyses data showed that a nanocrystalline phase of the anatase was formed after isothermal heating, of non-doped TiO_2 coatings (PDF78-2486), (Fig. 1). The XRD patterns of neodymium doped TiO_2 coatings show a decrease in the (101) peak intensity of the anatase phase, i.e. neodymium dopant suppresses the crystallization process. The sizes of the crystallytes also sligthly decreased: for the TP sample the sizes of the crystallites is 10 nm, while for Nd doped sample is 7 nm, respectively. Xiao et al. have demonstrated that the introduction of lanthanide dopant in TiO_2 results in a reduction in the size of the crystallytes, which is attributed to the segregation of doping cations at the grains inter-phase boundaries, thus suppressing the growth of nanocrystallites [5].

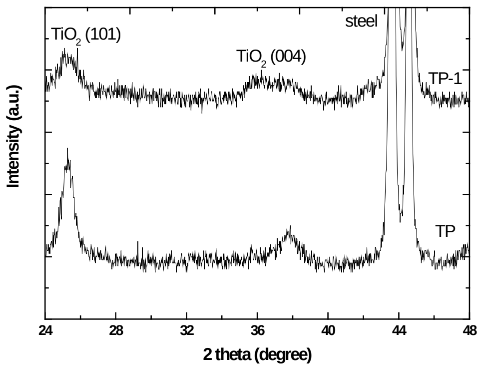

Fig 1 *XRD pattern of TiO_2 sol gel coatings.*

Figure 2 presents the XRD pattern of SC coating, which indicates the presence of cubic CeO_2 (crystallites size 6 nm) and SiO_2 crystallographic phases. The X-ray diffraction patterns of sample ST do not indicate the presence of a crystalline phase of TiO_2, so the sample has amorphous structure (it is not shown). The same result was obtained by Cheng and co-authors for sol-gel SiO_2 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% SiO_2 is amorphous.

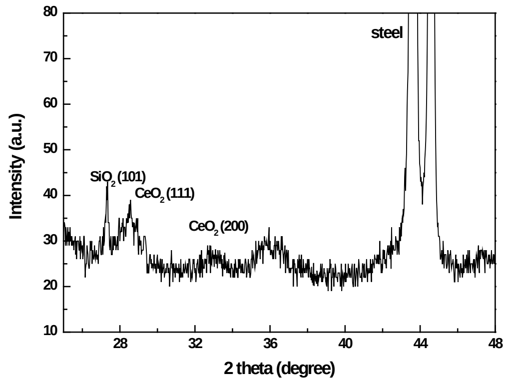

Fig 2 *XRD pattern of SiO_2/CeO_2 sample.*

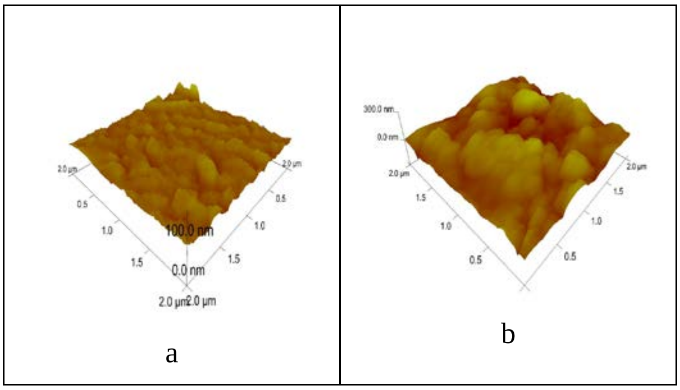

Fig 3 *AFM topography of fresh prepared TiO2 (a) and after corrosion test (b).*

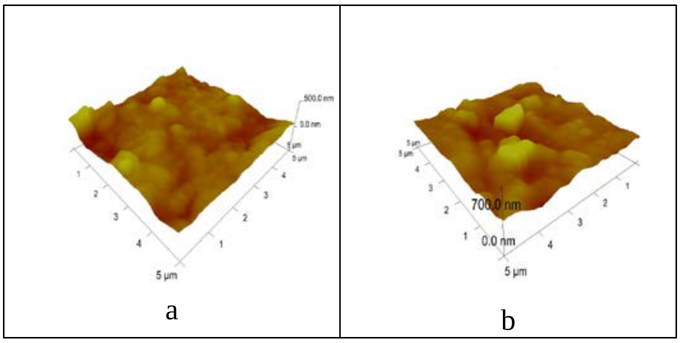

Fig 4 *AFM topography of Nd doped TiO_2 - freshly prepared (a) and after corrosion test (b).*

Figure 3 shows the topography of a TiO_2 coatings obtained from titanium isopropoxide fresh and after corrosion attack. The surface is relatively dense with numerous nano-sized crystallites. After the corrosion test the surface becomes rougher and pits are observable. The doping of titania coatings with neodimium leads to formation of much rougher surface than those of non-doped sample (Fig 4a). It consists of many crystalline aggregates. Corrosion process induces insignificant alteration of the surface morphology of doped samples (Fig. 4b). There are no visible pores and pits, which proved the corrosion resistance of the Nd doped TiO_2 samples. The same results were proved by the SEM analyses of the coatings (not shown here). Scanning electron microscopy of SiO_2/CeO_2 coatings reveals surface with many fine nanocrystals **(**Fig 5a) and the corrosion process does not lead to significant changes in the surface - cracks are not observable, which proves the high corrosion stability of this multilayer (Fig. 5b). Titania coatings are relatively dense and consist of larger superficial nanocrystals (Fig. 5c). The immersion in corrosive NaCl medium does not affects appreciably the nature of the surface – there are not any visible cracks; the roughness increases slightly (Fig. 5d).

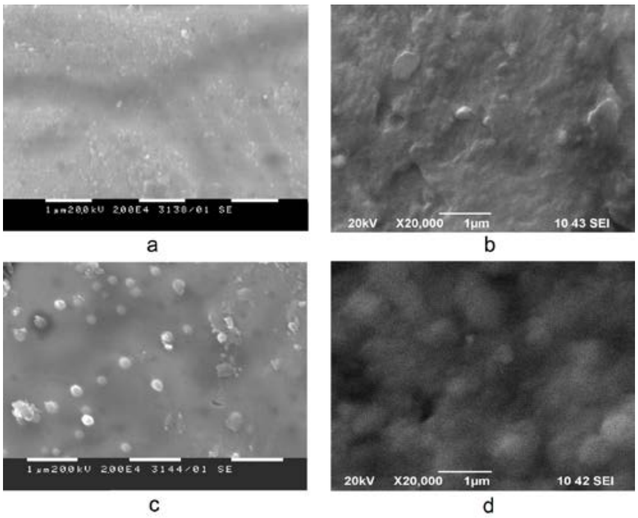

Fig. 5 *SEM photographs of SC -freshly prepared SC (a), SC -after corrosion test (b); ST- freshly prepared (c) and ST after corrosion test (d).*

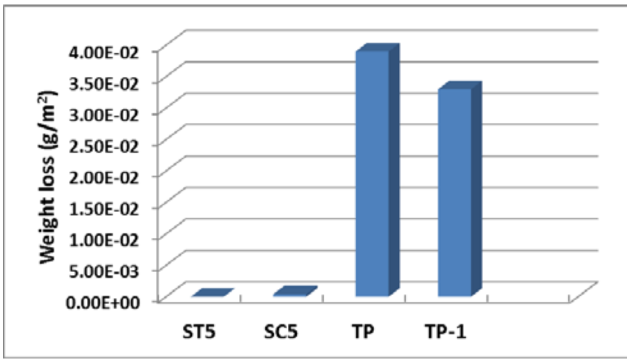

Fig. 6 *Weight losses of SiO_2/TiO_2 , SiO_2/CeO_2 multilayer and TiO_2 nondoped and Nd doped TiO_2 after corrosion attack.*

The corrosion resistances of SiO_2/TiO_2, SiO_2/CeO_2, non-doped and Nd doped TiO_2 coatings after 200 hours corrosion attack, estimated by the weight losses are shown in Figure 6. Zero weight loss was registered for titania deposited on SiO_2 after 200 hours in corrosive medium, while for the ceria/silica coatings weight loss id 4.10^{-4} g/m^2. The possible reasons for the anticorrosion action of Nd in TiO_2 can be explained by (i) the low degree of crystallinity of the titania coatings. According to the ref. [7] the improved barrier properties of TiO_2–CeO_2 composite is due to the presence of amorphous structure, which deteriorates the ion and electron conduction of the films (ii) the presence of rare-earth elements suppresses the cathodic oxygen reduction reaction as have been proved by et al. Fahrenholtz [8]. The CeO_2 and TiO_2 on SiO_2 layers exhibit much better corrosion resistance in comparison with one-component TiO_2 coatings. The possible reason for this behaviour is the low degree of crystallinity of the titania coatings, which improves their anti-corrosion properties. The obtained new bi-component coatings are promising with the view to increase the corrosion resistance of the steel,which gives the reason to extend the scope of the future experiments.

5. Conclusions

Several types of of nanosized coatings were prepared by sol gel methos: (a) one-component coatings -TiO_2 (b)Nd doped TiO_2 (c) bi-component layers, which consist of TiO_2 over SiO_2 (d) bi-component layers, which consist of CeO_2 over SiO_2. The XRD data revealed anatase phase for TiO_2 and Nd doped TiO_2 coatings. Ceria deposited on silica underlayer revealed well crystallized CeO_2 cubic phase, while TiO_2 deposited on SiO_2 has amorphous structure. The SEM and AFM studies show that the CeO_2 on SiO_2 bicomponent coatings have relatively dense surface. The TiO_2 coatings possess many surface nanosized crystallites. The corrosion resistance of the one-component and bi-component oxide coatings were evaluated by the weight loss after immerion in corrosive medium. The CeO_2 and TiO_2 coatings on SiO_2 exhibit better protective properties than the non-doped and Nd doped TiO_2 coatings as well as uncoated steel. The corrosion attack induces insignificant alteration of the surface morphology of both Nd doped TiO_2 samples and multilayer barrier coatings. The morphological and corrosion investigations proved that the bi-component oxide coatings on the base of titanium dioxide and cerium dioxide deposited on silica underlayer have perspective anticorrosion properties for various applications in industry.

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