Preparation of sol-gel SiO_2 coatings on steel and their corrosion resistance

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Abstract. A protective SiO_2 coating was prepared by sol-gel method on stainless steel plates, using precursor solutions having 2 different concentrations: low (0.5M) and high (2M) concentration. The dip coating-drying cycles have been repeated three times, after that the coatings were thermally treated at 300°C or 500°C in air. Scanning electron microscopy (SEM), AFM and X-ray diffraction analyses have been applied. The corrosion resistances of SiO2 coated steels were examined in NaCl medium for 346 hours. Many microcracks and craters in the samples, prepared from solution of high concentration appear after corrosion attack. The coatings obtained from solution of low concentrations reveals almost unchanged surface structure without visible cracks and pits. The evaluated corrosion rate of this coating is lower than those of uncoated steel.

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 with the selection of appropriate materials for particular application, by using 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 for the obtaining of thin films and coatings on metal surface, such as 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. Cost of precursor solutions has limited

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the use of sol-gel processing in many applications [17]. The sol–gel method is a wet-chemical technique and involving several stages: hydrolysis and polycondensation, gelation, aging, drying, densification and crystallization. The sol–gel technology is based on hydrolysis and condensation reactions [18, 19].

Typically the addition of catalysts increases the hydrolysis rate. The type of catalyst determines the pH of sols and affects the form of sol-gel materials, 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 received 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. Depending on heat treatment conditions, specially the final treatment temperature, the structure of sol-gel coatings may undergo changes. 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 is significant in 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 sol-gel method is an established method to produce homogeneous coatings with uniform thickness below 2μm [20]. Sol–gel technology has been significantly improved in the past 20 years. The sol–gel coatings are widely investigated in the area of optics [21], nanobiocomposites [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 limitations [26, 27]. Coatings with good passivity, insulating properties and good tribological properties show high corrosion resistance in aggressive eenvironment. Some papers [28-31] showed the feasibility of obtaining homogeneous and free of cracks sol-gel coatings on steel substrates. Other works [32] have demonstrated increases in the corrosion resistance by using zirconia or silica coatings.

The aim of this work is the obtaining of protective SiO_2 layers by sol-gel method (dip coating technique) on stainless steel plates and investigation their surface morphology, phase composition and chemical stability in salty solution of NaCl.

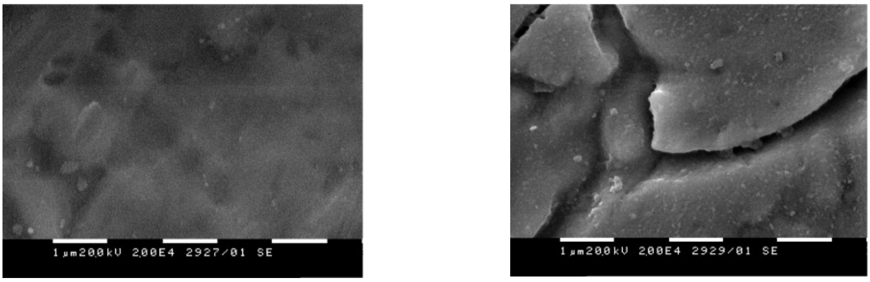
2 Experimental part

The preparation procedure of SiO_2 films by the sol– gel method was as follows: tetraethoxysilane (TEOS) wass dissolved into ethanol and stirred for 1 h. The mixture of ethanol, water and hydrochloric acid was added to the TEOS solution and also followed by stirring for 2 hours in order to obtain 0.5M and 2 M solutions. The mole ratio H_2O:TEOS was 3.7. The sample obtained from 0.5 M solution were denoted A, while the sample deposited from 2M solution were denoted B. The stainless plates AISI 316 were used as substrates. The substrates were cleaned ultrasonically in ethanol and acetone. The films were immersed in the corresponding solution and withdrawn at a constant rate of 3 cm/min and then were dried consequently at 60◦C and at 90°C. The samples A and B wre heated at 300°C. These steps were repeated 3 times. In order to study the effect of thermal treatment temperature on the protection properties, another sample denoted C produced from 2M solution was treated at 500°C for 1h. The phase composition of the samples was studied by X-ray diffraction (XRD) with CuKα-radiation (Philips PW 1050 apparatus). The average crystallite sizes of the films were estimated according to Scherrer's equation: The morphology of the coatings was investigated by means .of Scanning electron microscope PHILIPS SEM 515, (Belgium), operating at 20kV voltage. In order to study their chemical resistance the investigated samples as well as uncoated steel (reference sample) were exposed to the action of salty solution of 3.5% NaCl at 25°C (EN ISO10289/2006) in the course of 346 hours.The temperature of solution and the air temperature were controlled by calibrated thermometers. It was determined the mass weight loss after 256 and 346 hour.

3 Results and discussion

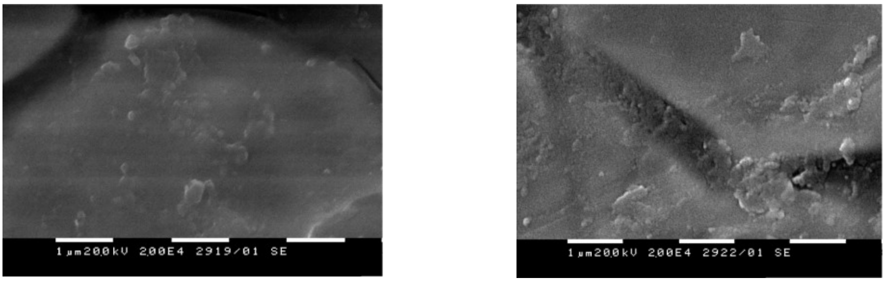
XRD analyses revealed that all samples are amorphous,since no sygnals of crystallized SiO_2 were observed. Several research groups were also obtained amorphous silica coatings thermally treated at 500ºC and 600ºC [33,34]

The SEM photographs of the substrate and silica coated steel before and after corrosion test ae shown in Figures 1-3.



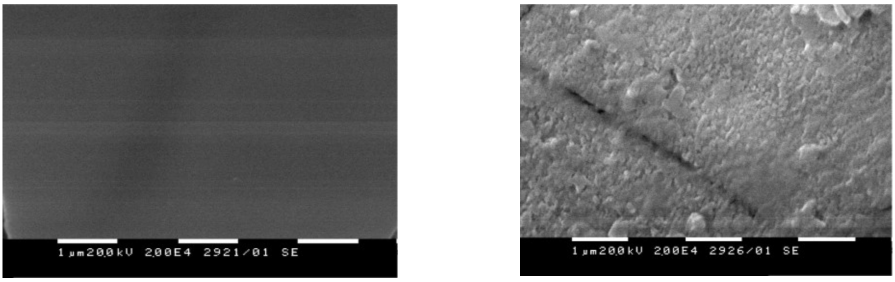
a b

Fig.1. SEM photographs of bare steel substrate a) before and b) after corrosion test.



a b

Fig.2. SEM photographs of sample A: a) before and b) after corrosion test.

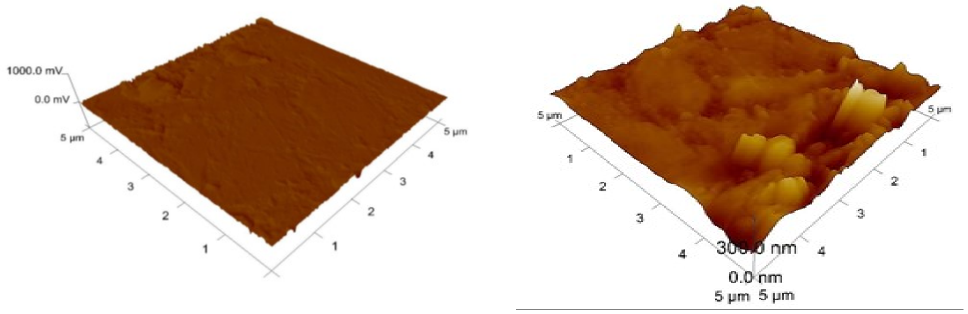


a b

Fig.3. SEM photographs of sample C: a) before and b) after corrosion test.

Figure 1 reveals the SEM images of steel substrate – bare substrate and after corrosion test. The films structure has been undergoing considerable changes during the corrosion test. Some cracks are clearly visible on the microphotographs. The silica films surface, prepared from 0.5 M TEOS solution is relatively dense with some crystal imperfections (Fig 2-a). Sample A preserves the surface structure without visible cracks and pores after corrosive attack. (Fig. 2-b) TEOS solution of high concentration leads to more flat surface of the coatings after treatment at 300 and 500ºC. After corrosion test there are many deep cracks in both samples B and C (Fig.3b). Sample C also reveals significant errosion of the surface.

Figure 4 represents the surface of SiO_2 coatings after corrosion test. On the surface structure of the sample A no visible cracks and pits are to be observed after corrosive test, but has some pitting effects (Fig 4-a). The roughness analysis gives the value Ra about 15 nm and Rq 24 nm for sample A after attack. The corrosive attack induces erosion of the surface and many cracks in the films, obtained from 2M TEOS solution. The film surface displays significant effect of corrosion. The roughness analysis of sample B gives the value Ra 20 nm and Rq 31 nm. There is appearance of microcracks and craters. (Fig 4-b). The erosion of the coatings becomes stronger after treatment at 500ºC, leading to eruption of some areas of sample C. Duran et al. have proved that the SiO_2 coatings, deposited on stainless steel and galvanized steel treated at 550ºC were more cracked because of the elimination of organic groups during the treatment reduces the plasticity of the coatings [33].



a b

Fig. 4. AFM images (3dimensional) of samples A (a) and C (b)

Acccording to DTA-TG analysis of the film A (Fig 5) exothermal and endothermal peaks are not registered.

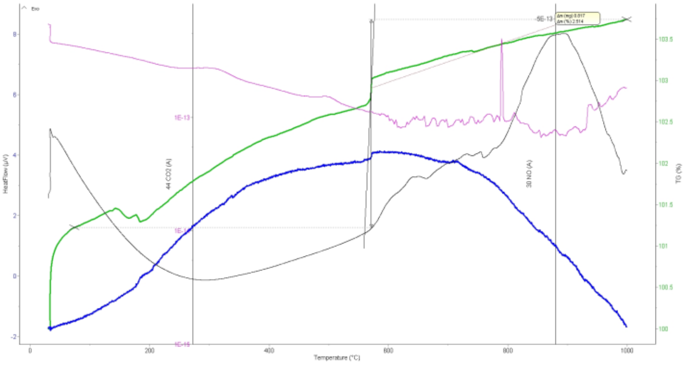


Fig. 5. DTA-TG analysis of sample A.

The weight losses of the and the uncoated steel and SiO_2 coatings (sample A) after 250 in the NaCl solution are 1.81 and 1.06 mg/cm^2, respectively. No weight changes were observed after 346 hours. As can be seen from Fig. 6 the weight loss increases up to 250 hours of the test, after that remains constant. It can be seen that the sample A exhibit the better protection properties in comparison to the uncoated steel.

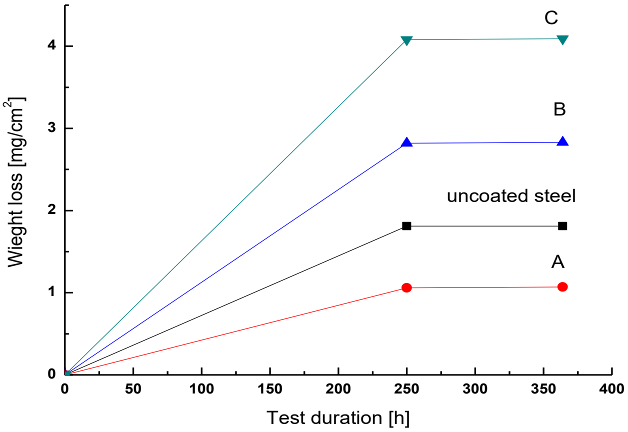


Fig. 6. Weight loss of the SiO_2 sol-gel coatings *vs* time.

The corrosion rate is based on the number of illimeters (thousandths of an inch) it penetrates each year. The corrosion rate was evaluated, according to the Standard - ASTMG31.

The corrosion rate of uncoated steel is 0.058mm/year, while for samples A, B and C are 0.035; 0.092 and 0.133mm/year, respectively. The obtained results revealed that the SiO_2 coatings, prepared from 0.5 M solution of TEOS exhibit the best protection properties. The formation of cracks is dependent on the internal stress in the coatings [18]. This effect is a result of the evaporation of large amount of solvents and organic residuals. Probably, in the samples produced from TEOS solution of high concentration (B and C) during the the thermal treatment the formation of cracks and pits are induced by the evaporation of the larger amount of intermediates (produced by hydrolysis). As a results the mechanical properties (hardness, plasticity etc) and the surface characteristics are deteriorated. This could be reason for decreased anti-corrosion properties. The application of TEOS solution of low concentration seemed more siutable for production iof SiO_2 coatings with enhanced corrosion resistance, due to their surface and mechanical characteristics.

4 Conclusions

Silica sol gel coatings, obtained from two different sol-gel solutions of low and high concentrations of TEOS and treated at 300ºC and 500ºC possess relatively dense surface. The protection efficiency of silica coatings decreases with the increasing of TEOS solution concentration. The coatings, deposited from 2M solution showed several microcracks and some erosion after immersing in corrosive medium regardless the treatment temperature. After corrosion attack, the sample, prepared from 0.5 M TEOS solution treated at 300ºC reveals almost unchanged surface structure. The corrosion rate of this coating is lower than those of uncoated steel.

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