PREPARATION OF SOL GEL SiO$_2$ COATINGS AND THEIR CHEMICAL STABILITY

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Abstract: Protective, SiO$_2$ layers were prepared by sol-gel method/dip coating technique/ on stainless steel plates. The precursor solution contains TEOS and ethanol with two different molarities. Hydrochloric acid was used as catalyst. The deposition-drying cycles have been repeated three times, after that the coatings were thermally treated at 300$^\circ$C or 500$^\circ$C in an air. Scanning electron microscopy (SEM) and XRD (X-ray diffraction) have been applied to investigate the surface morphology and phase composition. The chemical stability of SiO$_2$ coated steels were examined in NaCl medium.

Keywords: sol-gel method, dip coating technique, SiO$_2$-layers

1. Introduction

The major problem of corrosion occurs with steel as it is used as a structural material in industries like construction, automobiles, rail transport, bridges, infrastructure, shipbuilding, heavy industries etc. Corrosion of metal is seen as chemical and electrochemical degradation of metals or alloys due to reaction with their environment. Corrosion processes are accompanied by a number of reactions that change the composition and properties of the metal surface. Metal corrosion can lead to a severe decrease in the functionality and esthetics of metal products. Corrosion of metals 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. Corrosion control of metals is of economical, technical and environmental importance. Oxide films (Al$_2$O$_3$, SiO$_2$, TiO$_2$ and ZrO$_2$) and coatings can be deposited on metals to improve their surface 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 have limited 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$^\circ$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 various 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. Part of the driving force behind the growth of sol-gel coatings is the ability to make coatings with unique 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], nano bio composites [22], biomaterials [23], self-cleaning materials [24] and others [25]. Diffusion barrier, abrasion resistant, dielectric, metal or organic doped oxide coatings, and coatings with controlled porosity are some examples of other applications [17]. One of the most common causes of metal components failure is damage due corrosion. 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 good corrosion resistance in aggressive environment. 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 zirconium 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) was 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$_2$O: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 ethano land 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–2 hours and at 90°C for 1 hour. The samples A and B were 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 1 h. 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 signals of crystallized SiO$_2$ were observed. Several research groups were obtained amorphous silica coatings thermally treated at 500°C and 600°C [33,34] The SEM photographs of the coatings before and after corrosion test are shown in Figures 1-3. 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.

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The silica films surface, prepared from 0.5 M TEOS solution is relatively dense with some crystal imperfections (Fig 1-a). Higher concentration of TEOS solution leads to more flat and homogeneous surface of the coatings after treatment at 300 and 500°C (Fig 2 and 3, resp.). After corrosion test there are many deep cracks in both samples B and C (Fig 2b and Fig 3b). Sample C also reveals significant erosion of the surface. Sample A preserves the surface structure without visible cracks and pores after corrosive attack.

![Fig. 1 – SEM photographs of sample A: a) before and b) after corrosion test.](image1)

![Fig. 2 – SEM photographs of sample B: a) before and b) after corrosion test.](image2)

![Fig. 3 – SEM photographs of sample C: a) before and b) after corrosion test.](image3)

According to DTA-TG analysis of the film A (Fig 4) exothermal and endothermal peaks are not registered.

![Fig. 4 – DTA-TG analysis of sample A.](image4)

The weight loss of the SiO$_2$ coatings and the uncoated steel after 250 and 346 hours in the NaCl solution are shown in Table 1. No weight changes were observed after 250 hours. As can be seen from Fig. 5 the weight loss increases up to 250 hours of the test, after that remain constant.

It can be seen that the sample A exhibit the better protection properties in comparison to the uncoated steel.

![Fig. 5 – Weight loss of the SiO$_2$ sol gel coatings vs time.](image5)
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 - ASTM G31.

The corrosion rates 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 SiO2 coatings, prepared by dip coating method form 0.5 M solution of TEOS exhibit the best protection properties.

4. Conclusions

The SiO2 sol gel coatings, obtained from ethanolic solution of TEOS, treated at 300°C and 500°C possess relatively dense surface. The protection efficiency of silica coatings was decreased with the increasing of TEOS solution concentration. The coatings, deposited from 2M solution showed several cracks and some erosion after immersing in corrosive medium. After corrosion test, the surface of the sample, prepared from 0.5 M TEOS solution (A) remains almost unchanged. The corrosion rate of coating A is lower than those of uncoated steel.

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5. References