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Optical, Photocatalytical and Structural Properties of TiO_2-SiO_2 Sol-Gel Coatings on High Content SiO_2 Enamel Surface

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The TiO_2-SiO_2 optical films prepared from a sol-gel precursor were deposited on enamel surface using dip-coating techniques. The films were calcined different time from one hour till ten hours to investigate effect of calcination on self-cleaning and structural properties. Effects of film crystal structure, microstructure, photocatalytic activity and optical properties of the films were investigated using XRD, AFM and spectrophotometer and contact angle measurement. The TiO_2-SiO_2 dip-coating optical films calcined 1 h resulted in high structured surfaces, which were found to increase the photocatalytic activity.

Keywords: sol-gel, TiO_2-SiO_2, thin films, antireflection, photocatalysis, optical coating.

1. INTRODUCTION

Sol-gel coatings are widely used for a variety of technological and commercial applications as wear, corrosion [1], and high-temperature-resistant coatings [2] or with special functions for use in electronics, microelectronics, optics and chemistry [3, 4]. One of the potential areas is production of high capacity devices of solar energy (collectors) and a view to attain self-cleaning surfaces for mirrors, light (thermal energy) reflection and permeability regulating coatings for absorptive elements of solar energy – enameled steel tubes [5 – 7].

Over the last decade, sol-gel technology have focused on the binary oxide system studies, such as SiO_2-TiO_2 and ZrO_2-SiO_2, showing a good chemical and physical properties [8, 9], these coatings gained from different source materials and a wide range of oxide systems have been successfully used in sectors, such as optical sensors, laser technology and reflective coatings [10].

SiO_2-TiO_2 oxide nanostructure on the whole at a level is more effective photocatalyst than absolute TiO_2 [11], so can be used in solar energy collectors, and self-cleaning surface coatings out of organic compounds [12]. Sol-gel synthesis has become one of the most popular ways to synthesize mixed oxide material compositions.

Synthesis of sol-gel SiO_2-TiO_2 glass coatings is very attractive opportunity to acquire one of the most heat-resistant coatings having low linear temperature expansion coefficient (LTEC), as well as the increased chemical resistance to alkali corrosion [13].

This study is joined to investigate and get an idea of the opportunity to create a continuous enamel surface of the potential use of solar cells and photo-catalytic purposes with self-cleaning surface.

2. EXPERIMENTAL

The film deposition, morphology, surface structure and composition were investigated by atomic force microscopy (Veeco SPM II), X-ray diffraction (Rigaku Ultima+) and scanning electron microscope (SEM), film deposition was carried out with dip-coating (KN 4002 KSV NIMA Dip Coater Single Vessel System Small), optical properties was investigated by UV/VIS spectrophotometer (Shamidzu SolidSpec-3700) photocatalytic properties was investigated by UV lamp 125 W and UV/VIS photo spectrometer (ElmerPerkin LAMBDA 650).

The refractive index of TiO_2-SiO_2 thin films annealed different time was calculated from the measured UV-VIS transmittance spectrum. The evaluation method in this work is based on the analysis of UV-VIS transmittance spectrum of films deposited on non-absorbing substrate microscope slides. The refractive index $n(\lambda)$ over spectral range is calculated by using the envelopes that are fitted to the measured extreme:

$$n(\lambda) = \sqrt{S + \sqrt{S^2 - n_0^2(\lambda) n_s^2(\lambda)}}\ , \tag{1}$$

$$S = \frac{1}{2}(n_0^2(\lambda) + n_s^2(\lambda)) + 2n_0 n_s \frac{T_{\max}(\lambda) - T_{\min}(\lambda)}{T_{\max}(\lambda) + T_{\max}(\lambda)}\ , \tag{2}$$

where n_0 is refractive index of air, ns are refractive index of substrate, T_{max} is the maximum envelope and T_{min} is the minimum envelope [14]. The porosity of the thin films is calculated using the following equation [15]:

$$\text{Porosity} = (1 - \frac{n^2 - 1}{n_d^2 - 1}) \cdot 100\,(\%)\ , \tag{3}$$

where n_d is the refractive index of pore free anatase ($n_d = 2.52$), and n is the refractive index of the porous TiO_2-SiO_2 film.

The enamel (P15K45) that was used as a substrate were coated on stainless steel at 950 °C. The Enamel composition was: SiO_2 – 80 %, Na_2O – 8 %, Li_2O – 4 %, B_2O_3 – 2 % other adhesion forming oxides – 6 %. The P15K45 enamel contained the following components: pigment – 15 wt. % and crystalizator – 45 wt. % per 100 wt. % by weight of frit.

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The chemicals used for sol preparation were titanium (IV) isopropoxide (TTIP) (Sigma-Aldrich) as a precursor of TiO_2, tetraethyl orthosilicate (TEOS) (Sigma-Aldrich) as a precursor of SiO_2, 2-propanol (Sigma-Aldrich) as a solvent and hydrochloric acid (HCl) as a catalyst. TiO_2-SiO_2 sol was prepared by the hydrolysis of TTIP and TEOS with HCl. The preoperation order was as follows: TTIP and TEOS were firstly dissolved in 2-propanol and stirred 1 h, then both solutions were mixed and HCl was added. Then solution was stirred 30 min. The molar ratios of TTIP, TEOS, 2-propanol and HCl were 1 : 4 : 179 : 2.85, respectively. The deposition process was performed in a clean room at ambient environment parameters: 20 °C and 25 % the relative humidity.

The films were grown by dip-coating method on enamel (P15K45) [16]. The substrate was immersed in sol 3 times with a speed 220 mm/min and then dried at 200 °C and calcined in furnace 500 °C for one hour.

Dip-coating technique is a process where the substrate to be coated is immersed in a liquid and then withdrawn with a well-defined speed under controlled temperature and atmospheric conditions. An accurate and uniform coating thickness depends on precise speed control and minimal vibration of the substrate and fluid surface. The coating thickness is mainly defined by the withdrawal speed and the viscosity of the sol.

Photocatalytical properties were measured using distilled water solution of methylene blue (MB) for photodegradation. The initial concentration of MB in a reaction vessel was fixed at 10 mg/l. Before irradiation the samples were stirred for 30 min in the dark to reach absorption-desorption equilibrium. A 125 W UV lamp was used as a light source. During irradiation the samples were withdrawn at regular time interval and measured the absorbance spectra from 550 nm to 700 nm.

3. RESULTS AND DISCUSSION

3.1. Coating surface characteristic

Fig. 1 shows the XRD pattern of enamel (P15K45). Enamel shows four main crystal phases – tridymite, cristabolite, quartz phases are from enamel frit and chrome iron oxide comes from enamels pigment.

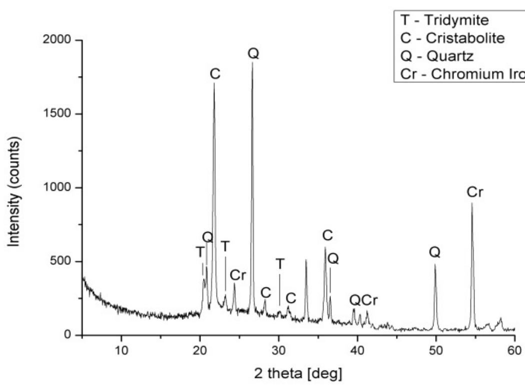


Fig. 1. XRD pattern of enamel (P15K45)

Fig. 2 shows the XRD patterns from TiO_2-SiO_2 coatings calcined at 500 °C 1 h and 10 h. It can be seen from Fig. 2 that the TiO_2-SiO_2 coatings annealed at 500 °C 1 h and 10 h show anatase and quartz phase. Increasing calcination time characteristic peak of anatase at $2\theta = 25.3°$ intensity of peak increases this can be seen in Fig. 3.

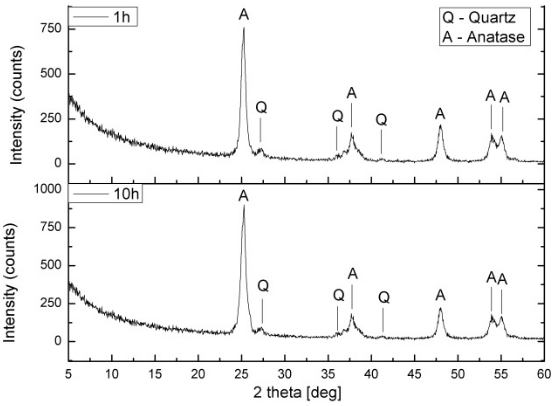


Fig. 2. XRD ptterns of TiO_2-SiO_2 sol annealed 1 h and 10 h

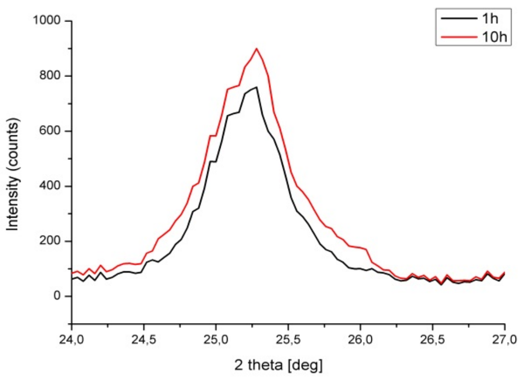
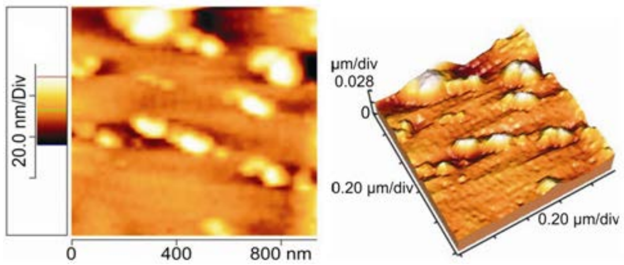


Fig. 3. XRD pattern of TiO_2 main peak of TiO_2-SiO_2 sol annealed 1 h and 10 h

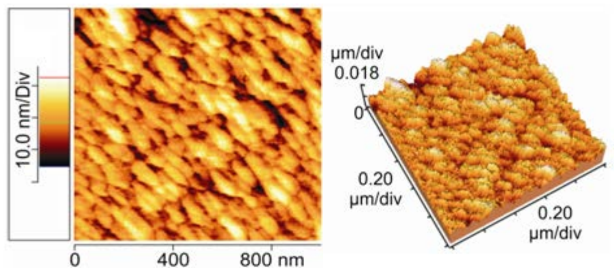
As shown in Fig. 4, surface morphology of enamel and TiO_2-SiO_2 coatings calcined at 500 °C and different calcination time 1 h and 10 h was investigated using atomic force microscopy. The particle size and average roughness of coatings are listed in Table 1. Particle size and roughness were measured from AFM images using Image processing v.2.1. program. From Fig. 4 and Table 1 we can see clearly that the films annealed for 1 h have smaller particles (65 nm) and lower average roughness (82.15) then coatings that were annealed for 10 h where particles size was around (95 nm) and average roughness (110.7 nm). It is well know that crystallite size is closely related to the calcination time, increasing duration of calcination increases the crystallite growth and its size [17, 18]. Fig. 5 we can see enamel and TiO_2-SiO_2 coating profilogramms, which shows structure with different roughness, which are presented in Table 1.

Table 1. Properties of the sol-gel coatings

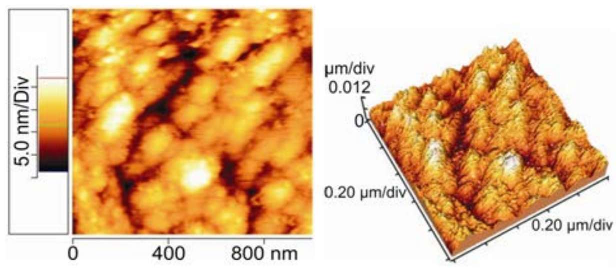
Sample	Average particle size (nm)	Roughnes	Refractive index (550 nm)	Porosity (%)
1 h	65.30	82.15	1.63	15.1
10 h	95.76	110.7	1.70	5.84



a

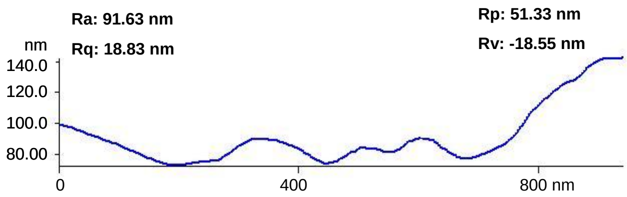


b

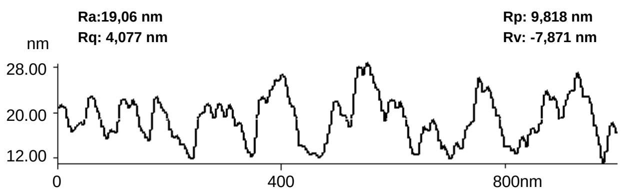


c

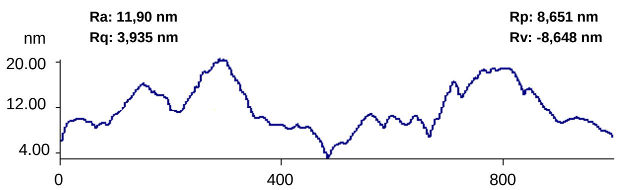
Fig. 4. AFM images: a – enamel; b – enamel + ST2 1 h; c – enamel + ST2 10 h



a



b



c

Fig. 5. Sol-gel coating profilograms: a – enamel; b – Enamel + ST2 1 h; c – enamel + ST2 10 h

Fig. 6 presents corelations between the average roughness and the contact angle. There can be seen that coatings with 1 h annealing show contact angle 38° and 10 h annealed coatings show 54°. Tamai and Aratani [19] reported that the increasing of average roughness increases the contact angle.

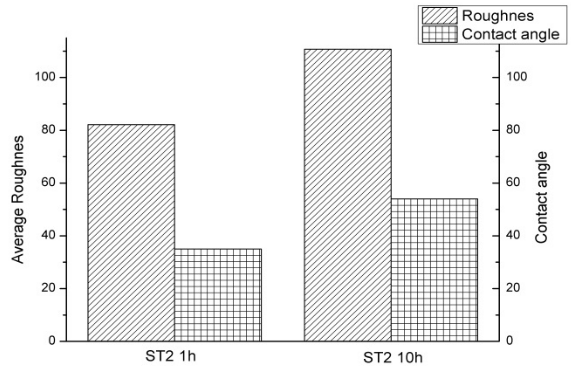


Fig. 6. Average roughness and contact angle of sol-gel coating

3.2. Optical properties

Transmittance and reflectance of the deposited coatings are shown in Fig. 7 and Fig. 8. Transmittance results (Fig. 8) show that the films annealed for 1 h have better transmittance in visible range 400 – 900 (average transmittance 91.7 %) then the coating annealed for 10 h (average transmittance 88.14 %). Difference in transmittance spectra one can explain by average particle size. In 1 h annealed coating particle size is smaller (65 nm) and does affect light transmittance, as much as in the coatings that where annealed for 10 h with average particle size (95 nm) that effect on light transmittance. Wangs and co-authors [20] have shown that the crystal size directly affects the light transmission, increasing crystal size decreases light transmission.

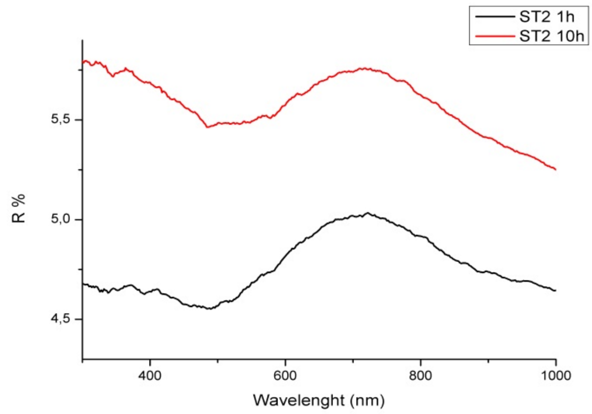


Fig. 7. Reflection spectra of sol-gel coating

The results refractive index and porosity of TiO_2-SiO_2 thin films calcined 1 h and 10 h at 500 °C are listed in Table 1. It is seen that refractive index increases from 1.63 to 1.7 with increasing calcinations time. On the other hand, the porosity decreases from 15.1 % at 1 h calcinations time to 5.84 % calcined 10 h. This is due to film densification and pore destruction in films during the calcination process. This findings confirm the similar work of Ug Ahn and coworkers [21].

From the reflectance spectra shown in Fig. 7 we can see that coatings annealed for 1 h have lower light reflectance (average reflectance 4.75 % in (400 – 1000) nm) then coating which annealed 10 h (5.58 % at (400 – 1000) nm),which means that 1 h annealed coatings are more perspective for application as anti-reflective coating [22].

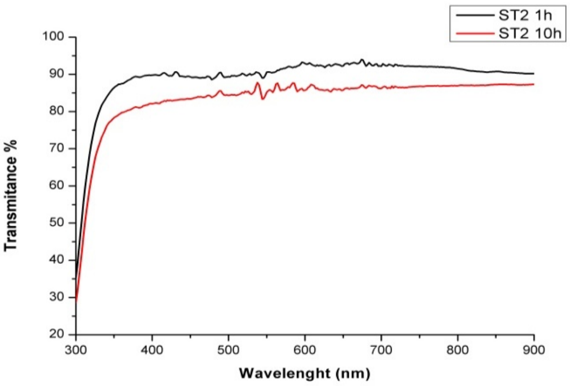
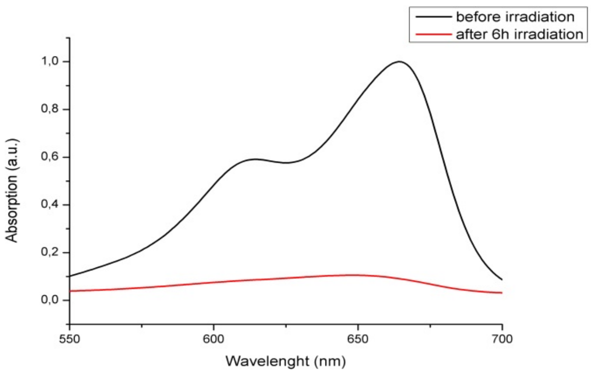
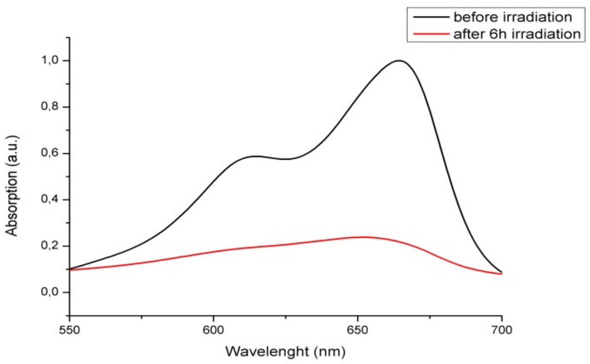


Fig. 8. Transmittance spectra of sol-gel coating



a



b

Fig. 9. Absorption spectrum of sol-gel coatings: a – ST2 1 h; b – ST2 10 h

3.3. Photocatalytical activity

Photocatalytic properties were determined from degradation of methylene blue solution. As can be seen from the commitment absorption curves (Fig. 9), the greater the degradation of MB was sample that has been calcined 1 h. As shown in (Fig. 10) sample which is calcined for 1 h is able to degrade the substance (MB) 89.7 % in 6 hours, while sample which calcined 10 h degrade 74.4 % of MB. This could be explained by the fact that the 1 hour calcined coating grain size is smaller (65.3 nm) while the 10 h calcined coating grain size reaches (95.76 nm). From literature data its well know that particle size have direct effect on photocatalytical activity. Xu and coworkers reported that photocatalytic activity of photocatalizator increases as the particle size of photocatalizator became smaller, especially when the particle size is less than 30 nm [23]. As well as reduced grain size increasing the specific surface area, increase in surface area probably causes a higher adsorptivity toward organic contaminants. Of course, the increase in surface content of hydroxyl groups will trap more holes in the valence band and thus prevent electron-hole recombination. [24].

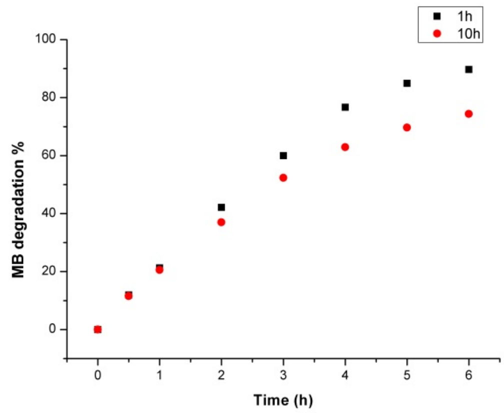


Fig. 10. Photocatalytical activity of sol-gel coatings

4. CONCLUSION

The TiO_2-SiO_2 composite thin films were prepared from precursor solutions and calcined different time. The coating microstructure, optical properties and photocatalytical activity of the films were studied. It was shown that the calcinations increase the grain size and decrease the surface area, we have described above – 1 h annealed coatings have 65 nm particles size but 10 h annealed coatings 95 nm, it leads to the increase of surface roughness. Increasing the grain size decrease light transmittance from 91.70 % with grain size 65 nm to 88.14 % with grain size 95 nm and increase light reflectance from 4.75 % for 1 h annealed coatings to 5.58 % for 10 h annealed coatings. It was found that calcination increases water contact angle of surface and decrease the porosity of thin films. One of the main aims of this study was to obtain photocatalytical coating which leads to self-cleaning surface. From our photocatalytical experiment results it could be concluded that 1 h annealed coating can degrade MO solution 89.7 % in 6 hours while 10 hours annealed coating 74.4 %. The photocatalytical activity is higher for 1 h annealed coating because it has smaller grains (65 nm) and higher surface area, so the photocatalytical activity increases with decrease the calcination time. This coating on enamel for stainless steel with the intrinsic properties like transmittance, low reflectance and photocatalytical activity is perspective composite to use in high solar power receivers.

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