

RIGA TECHNICAL UNIVERSITY
Faculty of Material Sciences and Applied Chemistry
Institute of Silicate Materials

Kaspars Mālnieks
Student of Doctoral study programme „Materials Science”

**ENAMEL MODIFICATION BY SOL-GEL COATINGS FOR THE
DEVELOPMENT OF THERMOTECHNICAL MATERIALS**

Summary of Doctoral Thesis

Scientific supervisor:
Prof., Dr. Habil. Sc. Eng.
G.Mežinskis

Riga – 2016

UDK 667.63(043.2)
Mā 405 e

Malnieks K. Enamel surface modification of sol-gel coatings for heat engineering material development. Summary of Doctoral Thesis.-Riga:RTU, 2016.-36 p.

Work printed in accordance with the RTU promotion council "RTU P-18" 2016.g. 16. march decision, protocol Nr.1.

ISBN 978-9934-14-900-9

**THE DOCTORAL THESIS IS SUBMITTED FOR AWARD OF A
DOCTORAL DEGREE IN ENGINEERING SCIENCE IN RIGA
TECHNICAL UNIVERSITY**

The thesis for the doctoral degree in engineering sciences will be publicly defended on 1st June 2016. At the Riga Technical University.

OFFICIAL REVIEWERS

Professor, Dr.Habil.Sc.Eng. Janis Grabis
Riga Technical University

Professor, Dr.Phys. Jānis Kleperis
Institute of Solid State Physics, University of Latvia

Dr.Phys. Janis Kalnacs
Institute of Physical Energetics

CONFIRMATION

I hereby declare that doctoral thesis submitted for the review to Riga Technical University to award of a doctoral degree in engineering sciences are independently written by me. The thesis has not been submitted to any other university for the award of a scientific degree.

Kaspars Malnieks (Signature)

Date:

The thesis has been written in Latvian and includes: introduction, literature review, methodological part, experimental results, and conclusions. The thesis has 153 pages contains 149 figures, 18 tables and a list of 147 references.

ACKNOWLEDGEMENTS

I would like to express my gratitude to all those who directly or indirectly have helped me in elaboration of doctoral thesis

First of all, I would like to thank my supervisor Professor Dr.Habil.Sc.Eng. Gundars Mezinskis for his the time, knowledge, support and understanding during the doctoral studies. Thanks for the inspiration to work in science.

I also wish to express my gratitude to my colleagues at the Institute of Silicate materials for the help, support and valuable tips during working time of writing. In particular, very much thank Ilona Pavlovska and Laimonis-Paul Bidermanis, for advice and a helping hand, you are to me as the "invisible" supervisors. Thanks also Inna Juhņeviča, Andris Šutka for their valuable advice.

Next, I would like to acknowledge the support of colleagues from the Institute of Technical Physics, RTU, the Institute of Polymer Materials, RTU, Institute of Physical Energetics and the Institute of Solid State Physics, University of Latvia for the opportunity to exercise equipment for materials research.

Finally, I would like to say a big thank you to my family and friends. Thank you for your encouragement, time, patience and invaluable support.

CONTENT

1. GENERAL DESCRIPTION OF WORK	6
THESIS TO BE DEFENDED	7
2. LITERATURE REVIEW	8
3. EXPERIMENTAL METHODS	9
4. REZULTS AND DISCUSSION	13
4.1. SOL-GEL COATING OPTIMAL DEPOSITION CONDITIONS	13
4.2. SOL-GEL COMPOSITIONS	17
4.2.1. TiO ₂ and TiO ₂ -SiO ₂ sol-gel systems.....	17
4.2.2. TiO ₂ -Fe ₂ O ₃ sol-gel system.....	18
4.3. XEROGEL INVESTIGATION	19
4.4. ENAMELS AND THEIR CHARACTERISTICS	20
4.5. ENAMEL WITH SOL-GEL COATING	24
4.5.1. Optical properties	26
4.5.2. Photocatalytic activity	27
4.5.3. Microhardness	28
4.5.4. Chemical resistance	28
4.5.5 Porosity.....	29
4.6 THERMAL RESISTANCE	30
CONCLUSIONS	32
PUBLICATIONS	33
CONFERENCES	35
REFERENCES	35

1. GENERAL DESCRIPTION OF WORK

Topicality of the research

Nowadays, more and more the world is meant for "green" energy or energy from renewable natural resources (sun, wind). The European Union (EU) has accepted a regulation that by 2020, 20% of EU energy consumption must come from renewable sources. Therefore, more and more pressing problem remains about the development of new and improved materials in the field of solar collectors.

Concentrated solar power (CSP) technology is used to produce a water vapor (heat) as well as electricity. Solar radiation conversion element in the CSP technology is heat radiation receptive coating on the heat-conducting surface, whose function is to receive a solar radiation. This coating is a multilayer structure which contains layers of high and low electromagnetic radiation absorption, refraction and emission coefficients. The production of such a material is complicated and expensive.

The coating of CSP collector must withstand temperatures in the range of 500 to 800°C, and must have a high corrosion resistance and minimal degradation in exploitation. These high requirements to CSP collector coatings currently both technologically and technically at the same time are not practically realized. Recent scientific literature has described a similar study results - conclusion – the stability of enamel of the solar collector materials reached only up to 450 °C.

The aim of the thesis

The thesis aims to develop a sol-gel coating for high-temperature resistant enamel on stainless steel with operation temperature up to 600°C.

The aim of the research

1. To synthesize the sol-gel coatings for high content SiO₂ borosilicate glass enamel on stainless steel;
2. To modify the TiO₂, TiO₂-SiO₂ sol-gel coatings with (TiO₂,Fe_xO_y) nanoparticles, providing the resulting coating with high chemical resistance, wettability, photocatalytical activity, as well as high thermal durability;
3. To create a borosilicate enamel on stainless steel with potential use in concentrated solar power collectors;

4. To analyze sol-gel and enamel coating structure and physico-chemical properties.

Scientific novelty of the research

The new innovative enamel with sol-gel coating which could be used in CSP is developed. High content SiO₂ enamel elaborated by the use of traditional enameling technology, capable to withstand 600°C during 3000 hours is manufactured. Enamel has low light reflection (~7%) from 300 to 2000 nm.

Practical importance of the research

The enamel with a high solar absorption, which provide low light reflectance (~7%), is developed for the first time in Latvia applying sol-gel coating which increased chemical resistance, reduced porosity of enamel surface and provided photocatalytic activity properties for that bilayer coating.

THESIS TO BE DEFENDED

1. TiO₂-SiO₂ sol-gel coating onto borosilicate enamel improves longevity maintaining it up to 600°C – providing high chemical resistance in an alkaline medium, maintaining a microhardness and low light reflection.
2. The enamel with low light reflectance (~7%) in the range from 300 to 2000 nm can be obtained using traditional enameling method applying pigment K6038 (chromium and iron oxide mix), and introducing CuO in the composition of enamel.
3. Applying a new sol-gel deposition method, which is based on several successive sol-gel coating layer deposition at room temperature (method 1x1x1), it is possible to achieve nanostructured TiO₂-SiO₂ sol-gel coating which provides high photocatalytic activity.

2. LITERATURE REVIEW

Sol-gel coatings are very promising and widely used in various industries (for example, optical coatings, solar cells, solar collectors, etc.). Over the past decade, studies of sol-gel materials have made it possible to use these coatings for a very wide range. However, one of the most important sectors is the industry of optical coatings, where owing to the sol-gel technology, these coatings are able to provide a much higher quality compared to other methods. Sol-gel coatings were obtained with a variety of raw materials and a wide range of oxide systems has already been successfully used in such sectors as optical sensors, laser technology and anti-reflective coatings [1]. Over the last decade, sol-gel technology have focused on the binary oxide system studies, such as $\text{SiO}_2\text{-TiO}_2$ and $\text{ZrO}_2\text{-SiO}_2$, showing a good chemical and physical properties and makes it possible to apply the coatings in still unexplored sectors such as electronics where transparent, stable and environmentally friendly transistors can be created [2]. $\text{SiO}_2\text{-TiO}_2$ oxide formed nanostructure is more effective photocatalyst than absolute TiO_2 [3], so it could be used in solar energy collectors as self-cleaning surface coatings against organic compound polluting effect. In turn within $\text{ZrO}_2\text{-SiO}_2$ systems zirconium oxide plays an important role which gives to coatings a higher corrosion resistance, increases the coating hardness, and chemical resistance in acidic and alkaline conditions [4].

To achieve efficient use of low-intensity energy such as normal solar radiation, which would allow warming up a variety of fluids (water, air or specific heat carrying liquids) or producing vapor, there is a need for effective energy collection and storage, which could be most economical. Therefore, a variety of solar collectors and energy storages systems are used for absorption of solar radiation. In some occasions even solar concentration mirrors are applied, which allow to increase the solar collection efficiency, but also increases the collector operating temperature from 300 to 500 °C, such collectors are known as parabolic or concentrated solar power (CSP) collectors. Most of the collectors are flat collectors which are operating at relatively low temperatures (usually up to 100°C), except hot summer periods, when temperature can reach up to 200 °C [5,6].

Concentrated solar power systems use solar energy absorbers to convert solar radiation to thermal energy. A CSP research is aimed to reduce the cost of parabolic solar collectors. One of the approaches is to increase the operating temperature of the solar coatings from approximately 400 °C

to 500 °C or higher. To accomplish this, new more efficient selective coatings are needed that have both high solar absorbance and low thermal emittance at 500 °C. Although such coatings are used in evacuated environments, the coatings need to be stable in air in case the vacuum is breached. Currently available coatings do not have the stability at desired operating temperatures. For efficient photothermal conversion solar absorber surface must have high solar absorbance (α) and low thermal emittance (ϵ) at the operational temperature. [7].

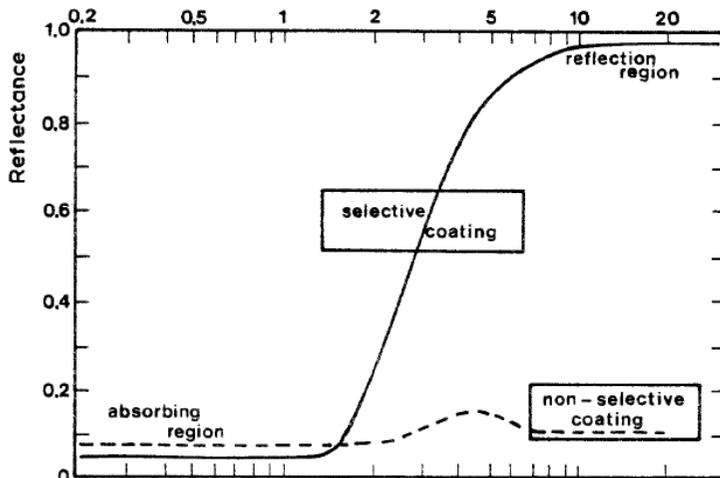


Figure 1. Selective coating [8]

3. EXPERIMENTAL METHODS

For sol preparation reagents are used, which are labeled as „chemically pure”. Tetraethylorthosilicate 98% ($C_8H_{20}O_4Si$ – TEOS, SIGMA-ALDRICH), titanium (IV) isopopoxide 98% ($C_{12}H_{28}O_4Ti$) – TTIP, Fluka), iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$ SIGMA-ALDRICH), isopropanol (C_3H_7OH , SIGMA-ALDRICH), glacial acetic acid (CH_3COOH - HOAc, ACROS), ethylene glycol ($C_2H_6O_2$ SIGMA-ALDRICH), and titanium (IV) oxide, anatase (particle size < 25 nm, SIGMA-ALDRICH) were used.

Synthesized sol-gel compositions are summarized in Table 1. sol preparation scheme is shown in Figure 2.

Table 1

Best sol-gel compositions

Composition name	Component composition (mol)					
	TEOS	Ti (IV) propoxide	Isopropanol	CH ₃ COOH	H ₂ O	FeCl ₃ * 6H ₂ O
T1	-	1	10	0.5	-	-
T2	-	1	10	1	-	-
T3	-	1	10	2	-	-
T4	-	1	5	4	-	-
T5	-	1	10	4	-	-
T8S2	0.2	0.8	5	3.2	0.1	-
T6S4	0.4	0.6	5	2.4	0.1	-
T4S6	0.6	0.4	5	1.6	0.1	-
T2S8	0.8	0.2	5	0.4	0.1	-
TFe ₁	-	1	10	4	-	0.1
TFe _{2.5}	-	1	10	4	-	0.125
TFe ₅	-	1	10	4	-	0.15
TFe _{7.5}	-	1	10	4	-	0.175
TFe ₁₀	-	1	10	4	-	0.2

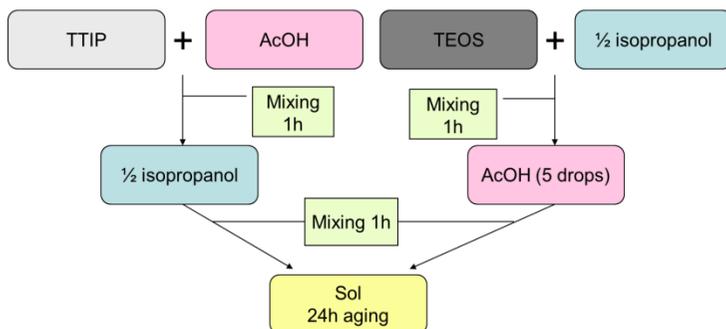


Figure 2. Scheme of sol preparation

After the synthesis of sols, they were aged and deposited onto enamel and glass slides by the use of dip-coating technique with speed (30-220 mm/min) and annealed at 500°C according to the scheme shown in Figure 3.

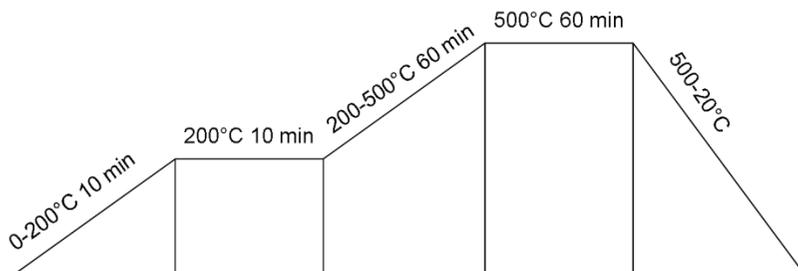


Figure 3 Heat treatment regime

Enamel coatings were applied onto chromium-nickel steel alloy by slip-casting method. Metal substrate enamelling was performed using frit prepared with different grinding additives and pigment K 6038 (chromium and iron oxide mixture) ratios against frits mass.

Frit composition (mass %)

- SiO₂ – 83 %;
- B₂O₃ – 7 %;
- Li₂O – 6 %;
- MnO – 3%;
- CoO – 1%.

Preparation of steel:

- Steel sheets were divided into smaller units with size (2x1) cm.
- Surfaces of acquired plates cleaned from oxides and fat by firing in the oven at 900°C (5 min).
- Sintered plates cleaned with sandpaper to the metallic shine.

Slips preparation:

- Slip were prepared from the above mentioned composition of frit and water,
- Take mortar, pour the frit and add water, stir everything together until a homogenous mass with a certain consistency for enameling is formed.

Enamelling:

- On the pretreated substrate the slip is deposited and then dried in an oven for 10 minutes at 100°C,

- After the sample was dried it is was inserted in an oven to anneal it for various times at 925 °C. Time depends on the type of enamel and was between 10 and 2 hours.
- After firing the sample was cooled to room temperature.

Table 2

Chemical composition of enamel

Enamel	Enamel composition mass %	Condition of crystallization
E1	SiO ₂ frit Nr 1. – 100 Pigment – 10-100	After the final enamel layer was reached the samples remained at 925 °C/2 h
E2	SiO ₂ frit Nr 1.– 100 Pigment – 10-50 Crystallization – 10-50	
E3	SiO ₂ frit Nr 2. – 100 Pigment – 10-70 Grained sands (SiO ₂) – 10-70	After the final enamel layer reached the samples remained at 925 °C/10 min
E4	SiO ₂ frit Nr 3. – 100 Pigment – 10-70 Grained sands (SiO ₂) – 10-70 CuO – 10-50	

Various analysis analysis to determine number of parameters were performed when the samples were prepared. .

Coating homogeneity was estimated by optical microscope M 420 (Leica Wild Makroskop), to find out optimal deposition and annealing conditions of the sol-gel coatings.

The crystalline phases of enamels and sol-gel coatings was determined by the X-ray diffraction (XRD) analysis (Rigaku Ultima+, Japan).

By the use of atomic force microscopy (AFM) and scanning electron microscopy (SEM) the surface microstructure of coatings was studied.

Chemical durability of enamels and enamels with sol-gel coatings was determined out with enamels. Chemical resistance was tested against the alkaline environment according to ISO 28706-4:2008. Test was carried out with 0,1 molar NaOH solution.

Sol-gel coating photocatalytical properties were measured using the solution of methyl orange with concentration of 0,01 g/l. Samples were irradiated with UV lamp (dpk-120) 125 W 365 nm.

Thermal stability of enamels was evaluated both for enamels and enamels with sol-gel coating. Thermal stability test conditions: 600°C in air. The samples had to withstand at least 3000 hours. After thermal stability test, samples were examined by XRD, AFM, UV-VIS spectroscopy and chemical resistance test, and the obtained results were compared with results obtained before thermal stability test.

Optical properties (light reflectance, absorption) and light transmittance was determined using UV-VIS spectrophotometer Shimadzu SolidSpec - 3700 and Thermo Scientific spectrophotometer Genesys 10s UV-VIS. Light reflection and absorption was measured in the wave range from 300 to 2500 nm.

4. RESULTS AND DISCUSSION

4.1. Sol-gel coating optimal deposition conditions

Sol-gel coatings were deposited at various speeds in the range of 30 mm / min to 220 mm / min. From the results shown in the table 3 it could be concluded that the increase of coating deposition speed of deposition causes the increase of coating thickness. Coating thickness also affects the quality of the coating, as the greater the thickness of the coating, the higher the chance that coatings will crack or settle and lose the adhesion to substrate. During these experiments, it was observed that the coatings started to crack if their thickness was more than 150 nm. Coating cracking is related to the evaporation of the liquid phase from coating and internal stresses, resulting in coating during firing.

Table 3
Coating thickness depending on the deposition speed

Deposition speed (mm/min)	30	45	60	90	120	150	180	220
Coating thickness (nm)	~90	~111	~130	~156	~210	~235	~255	~280

Different calcination modes were studied in order to determine the optimum coating heat treatment in, the maximum sintering temperature, heating rate, and the duration of calcination. Three different calcination

temperatures 450, 500 and 550°C were used during experiments. To evaluate the effect of particulate temperature on the coating formation, and to find out necessary temperature at which desired crystalline phase was formed (anatase TiO₂ in the case of sol-gel coatings) XRD experiments were carried out.

As can be seen from Figure 4 in the coating which calcined at 450 ° C, no crystalline phase was established , coating is X-rays amorphous, while in the coatings, which have been calcined at 500 and 550 ° C anatase is found as only one crystalline phase . The difference between 500 and 550 ° C calcined coatings is that for 550 ° C calcined sample there is an increase in intensity of identified crystalline phases, which shows that larger crystallites or crystals are developed in the coating. As the crystal size has an effect on the photocatalytic properties, samples were annealed at 500 ° C in the further work.

The rate of oven temperature rising is also important to coating calcination, as it affect both the crystal size and the rate of evaporation of the liquid phase in the coating, which affects coating adhesion and homogeneity. According to research carried out we chosed 5 ° C / min rising rate of furnace temperature as optimal.

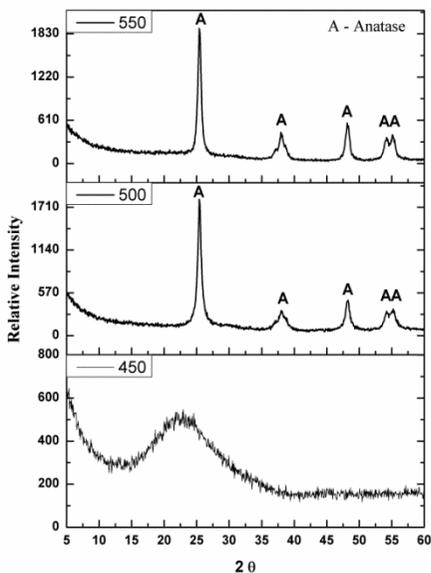


Figure 4. XRD patterns of TiO₂ sol-gel coatings at different calcination temperatures

Investigating optimal calcination time at 500°C of coatings the studies were performed, where the samples were calcined for 30 min, 1, 3, 5, 7, and 10 hours. After calcination coating samples were studied by AFM. According to the results of the AFM studies (Fig. 5.) it could be detected that no typical particles or crystallites on the surface of the coating calcined during 30 minutes could be observed, while for sample calcined during 1h there are visible particles on the surface with dimensions of 60-100 nm. In coatings which were calcined for longer time particles observed on the surface grew larger and formed agglomerates.

Creating multi-layer coatings 2 methods were used (3x and 1x1x1). Coatings which obtained drying each layer at 200°C and then calcinated at 500 °C (3x) and coatings, obtained by drying each layer at ambient temperature and then calcinated at 500°C (1x1x1) were investigated by AFM.

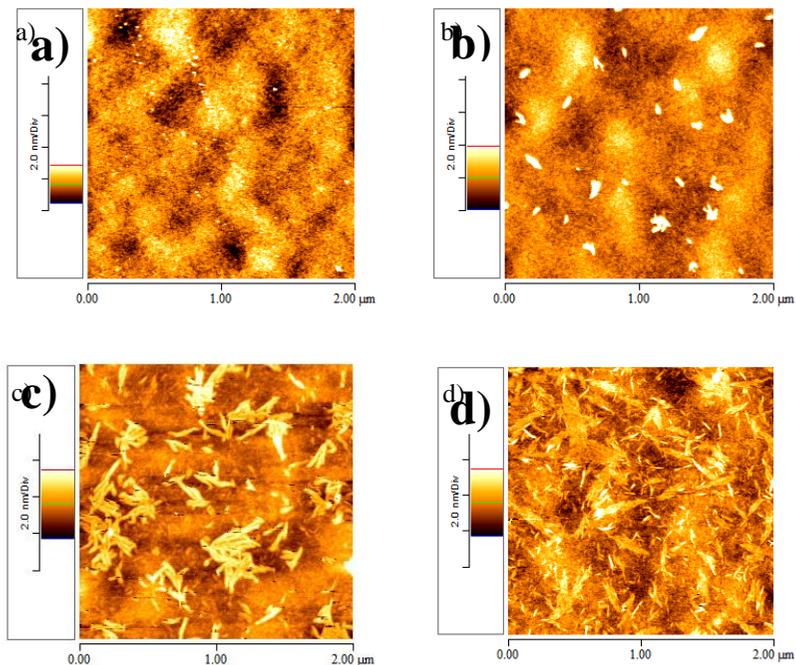


Figure 5. AFM results of calcined coatings a) 30 min; b) 1h; c) 5h un d) 10h

Comparing AFM images it can be seen that in the coating obtained with 3x method (Fig. 6.). Particles and particles agglomerates were formed. . In turn, there are particles with dimensions of $\sim 100\text{nm}$ in the coating obtained by the method of 1x1x1 (Fig.7.). These differences may be related to the fact that in the coatings obtained with 3x method after the drying of each coating layer the possibility of one or more nucleation events randomly distributed over the surface of the amorphous regions of the film was allowed. After a nucleus was formed, the next dip-coating cycle contributes further to the mass of nuclei, resulting in the growth of crystallite agglomerates. Such agglomerates in structure effects other coating properties such as light transmittance and photocatalytic properties.

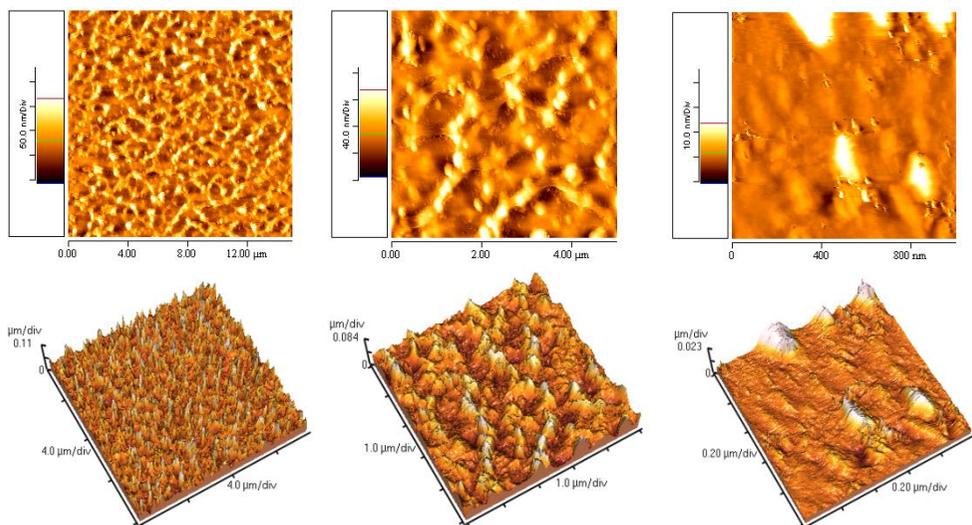
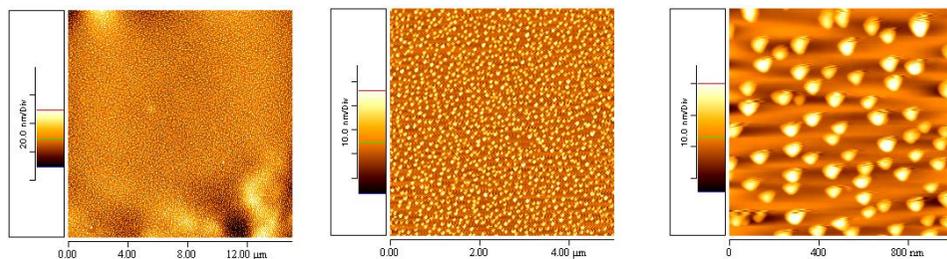


Figure 6. AFM images of 3x coating.



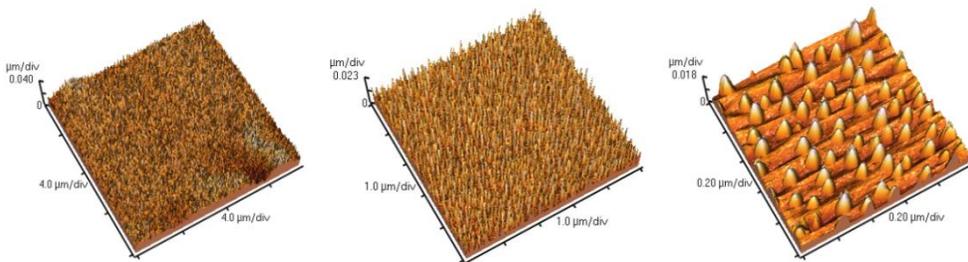


Figure 7. AFM images of 1x1x1 coating.

Basing on the results obtained the coating method (1x1x1), by a deposition speed (45 mm / min), calcination in oven at 500 ° C for 1 hour with temperature rising rate of 5 ° C / min. was selected for further work.

4.2. Sol-gel compositions

A variety of sol-gel compositions with a variety of components and their molar ratio were used at work. Some of synthesized compositions are summarized in Table 1. Basically 3 different sol-gel systems: TiO₂, TiO₂-SiO₂ and TiO₂-Fe_xO_y were used. Optimal compositions were selected from all compositions, which was later applied to the enamel surface.

4.2.1. TiO₂ and TiO₂-SiO₂ sol-gel systems

Comparing two sol-gel systems the characteristics of the light transmittance and photocatalytic activity of were chosed as a basis. Comparing two systems it could be seen that the TiO₂-SiO₂ sol-gel coatings (T8S2) have better photocatalytical activity (88%) comparing to the TiO₂ sol-gel coatings (T5) – 80%. As well as light transmittance of T8S2 is better (83-92% in the range from 300 to 2500 nm) than that for the T5 coating (80 to 89% in the range from 300 to 2500 nm), as it could be seen in Fig. 8.

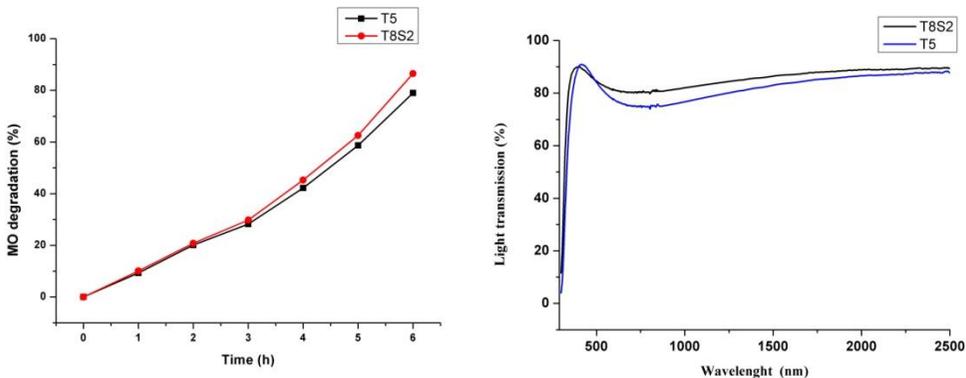


Figure 8. Photocatalytic activity and light transmittance of T5 and T8S2 coating.

Such differences in parameters can be explained by coating microstructure and grain size on the surface of the coatings. The crystal size of T5 coating was $\sim 85\text{nm}$ while for T8S2 coatings the crystal size was $\sim 60\text{ nm}$. This affects both the light transmittance and photocatalytic activity as it is known from the literature data that photocatalytic activity in coatings depends on the size of crystallites on the surface - higher photocatalytic activity is for smaller the crystallites on the surface [9].

4.2.2. $\text{TiO}_2\text{-Fe}_2\text{O}_3$ sol-gel system

In titanium –iron systems TTIP and iron (III) chloride hexahydrate as Fe_2O_3 precursor was used. Several compositions with relatively low iron content (0,1-10 mol%) within this system were synthesized. Compositions are shown in Table 1. The role of Fe^{3+} ions in this system was to replace Ti^{4+} ions in the lattice of anatase and to improve the photocatalytic activity in visible light. During experiments it became clear that the best composition regarding the photocatalytic activity was composition with 5 mol% of iron oxide, as adding smaller amounts of iron oxide, coatings did not showed photocatalytic activity in the visible light spectrum. Coatings with 5 mol% of iron oxide were able to degrade 40% MO in 6 hours at visible light. While the light transmittance was lowest (73 to 87% in the region from 300 to 2500 nm), as it can be seen from Fig. 9.

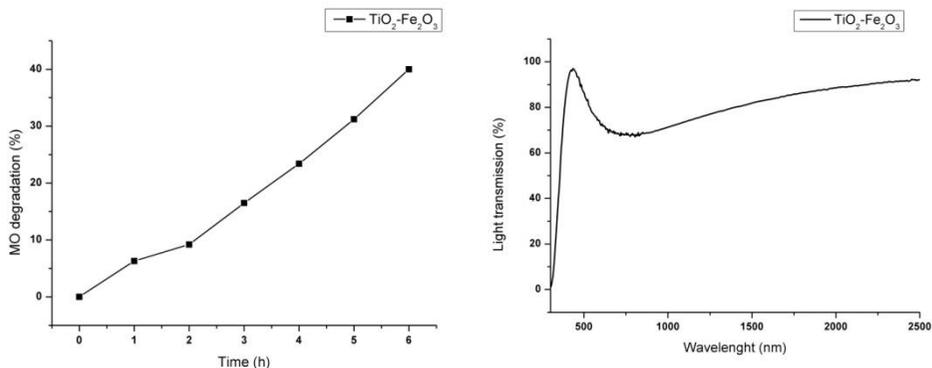


Figure 9. Photocatalytic activity and light transmittance of $\text{TiO}_2\text{-Fe}_2\text{O}_3$ coatings.

4.3. Xerogel investigation

Xerogels were studied with the aim to find out the change of crystalline phases which takes place at 600°C . This temperature was chosen because the working temperature of enamel with sol-gel coating will be 600°C . Such studies were not possible for coatings on glass slides, because slide softening temperature is $\sim 560^\circ\text{C}$. After xerogels heat treatment, which was exactly the same as for coatings, only calcination temperature was 600°C they were investigated by XRD. From XRD data it could be concluded that in TiO_2 and $\text{TiO}_2\text{-Fe}_2\text{O}_3$ xerogels a new crystalline phase – rutile formed. Such shift of crystalline phase affects photocatalytic activity, which decreases and light transmission also is reduced. However in the $\text{TiO}_2\text{-SiO}_2$ case, such phase formations did not occurred (Fig. 10.), and only one crystalline phase, which is detected in XRD patterns was anatase, just as it was at 500°C calcined samples. Similar results have been published in other researcher works giving evidence that by addition of SiO_2 to TiO_2 system it is possible to maintain anatase phase at temperature higher than 500°C [10]

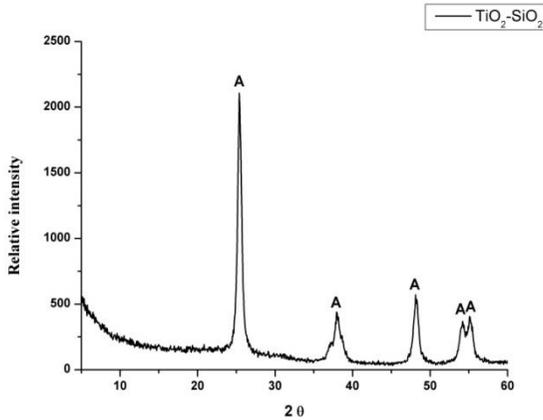


Figure 10. XRD patterns of $\text{TiO}_2\text{-SiO}_2$ xerogel, calcined at 600°C

4.4. Enamels and their characteristics

High SiO_2 content borosilicate glass enamels on chromium nickel steel were used in the study. Different compositions of frits used are shown in Table 2. To get black painted, expanded surface of enamels their frits were mixed with mill additives. Various mill additives / ground sand / pigment relations were used for ground sand (SiO_2) and pigment K 6038 (chromium and iron oxide s mixture). In the case of enamel E2 specially prepared crystallizer consisted of grinded sand SiO_2 and 3% soda Na_2CO_3 was added s. Also in the series of enamel E4 compositions different visible light absorbing oxides (CuO , FeO and MnO).were added. To obtain characteristics of enamels and to choose best enamels for thermotechnical materials after the synthesis of enamels these have been investigated by the use of various methods (AFM, SEM, XRD, UV-VIS spectroscopy).

One of the main characteristics was the surface structure, which affect the reflectance of light (Fig.11). The surface roughness was investigated by AFM, the results are shown. As seen from the table the smallest surface roughness is characteristic for enamel E2 ($0,91 \mu\text{m}$) while highest surface roughness for enamel E4 ($1,47 \mu\text{m}$) which directly affects enamel light reflection. Enamel light reflectance spectra are shown in Fig. 12.

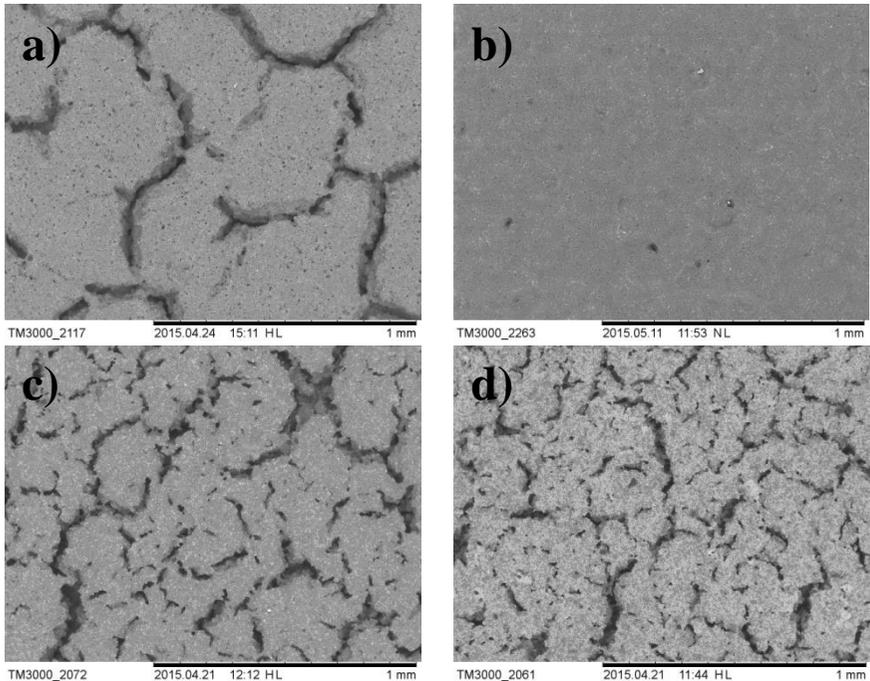


Figure. 11. SEM microphotographs of enamel surface: a) E1 b) E2 c) E3 and d) E4.

Table 4

Enamel surface roughness

Sample	E1	E2	E3	E4
Surface roughness (μm)	1,11	0,91	1,47	1,47

Since light reflection is a main characteristic of CSP materials, then basing on reflectance spectra enamels E3 and E4 were chosen as potentially best enamels (Fig. 12). For the best enamels as optimal annealing temperature (950°C) was determined. For the enamel E4 as the optimal CuO amount which gave the lowest light reflections also was determined. That was 30 parts of CuO by 100 parts of frit. As can be seen from surface roughness data of enamels E3 and E4, these should have similar light reflectance, however these are quite different. That is why the extra CuO amount added to enamel E4 acted as the donor of cation, while pigment acted as the donor

of anions for spinel which formed in enamel. Such an explanation is based on XRD data obtained. XRD results (Fig. 13,14.) shows that enamel E3 has four crystalline phases – quartz, spinel, chromium iron oxide and aegerine formed from pigment which was added in the composition of enamel. While enamel E4 has just two crystalline phases – quartz and spinel, whereof it can be concluded that CuO acts as a cation in the formation of spinel.

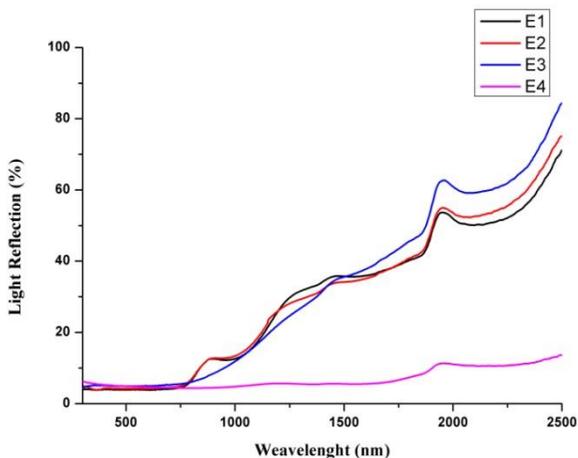


Figure 12. Light reflectance spectra of enamels E1, E2, E3 and E4.

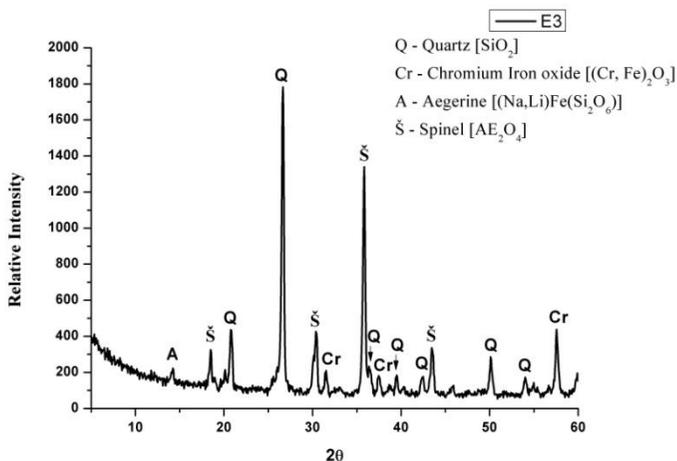


Figure 13. XRD pattern of enamel E3

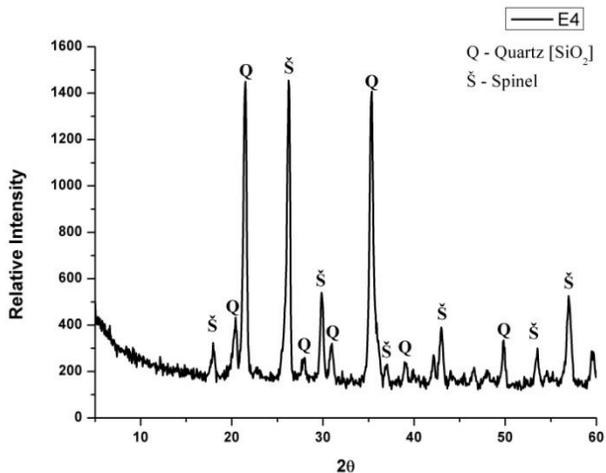


Figure 14. XRD pattern of enamel E4

SEM studies of enamel E3 and E4 surfaces confirmed XRD results, because as shown in Fig 15. On the surface of enamel E3 is the insignificant amount of white crystal agglomerates, while the surface of enamel E4 is almost completely covered with the crystal agglomerates of spinel crystals that has been formed on the surface of enamel.

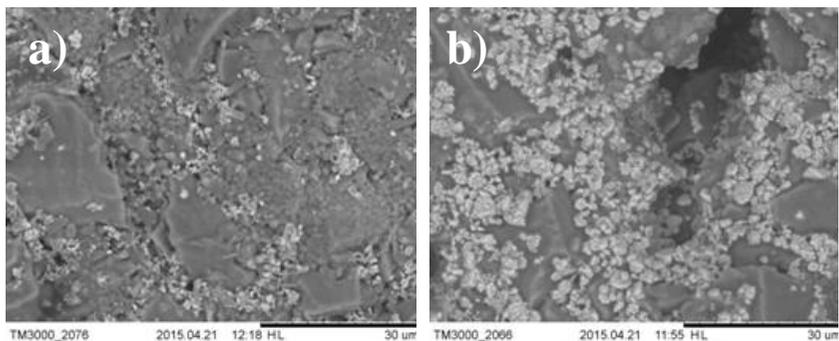


Figure 15. SEM microphotographs of enamel surfaces: a) E3 and b) E4.

As an additional characteristics of best enamels surface porosity or pore distribution was determined by mercury porosimetry. Two pore sizes 5-40 μm and 100-1000 μm were dominated for both enamels by. In the addition of enamels porosity, also surface contact angle was measured, which could

not be determined for enamel E3 and E4 because these enamels were too porous.

4.5. Enamel with sol-gel coating

After sol-gel coatings were investigated and evaluated, for future work was used sol-gel coating T8S2 which was deposited on enamel with optimal deposition speed and optimal calcination regime. After coating deposition, coating surface was investigated with AFM results can be seen in Figure 16. As shown in results that coating structure is different on different enamels, this could be explained by different enamels morphologies.

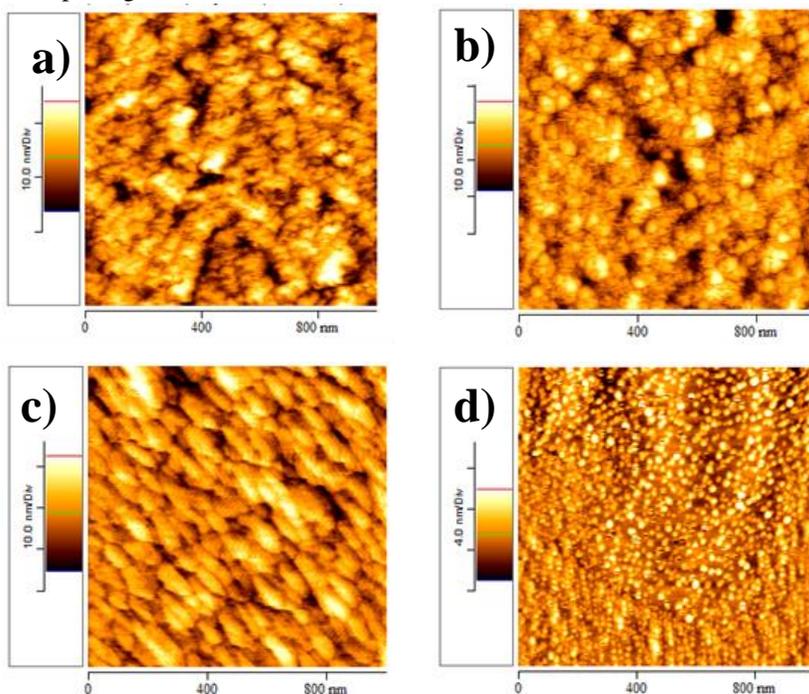


Figure 16. AFM results of enamels with sol-gel coating T8S2 a) E1 enamel, b) E2 enamel, c) E3 enamel, d) E4 enamel

To judge on the formation of crystalline phases in coatings deposited on enamel, these were investigated by XRD. X-ray diffraction results of enamel E4 which are shown in Fig.17 identify the crystalline phase of anatase, in contrary to that what has been observed after sol-gel deposition on glass

slides. This could be due to the fact that the sol-gel coating was deposited onto enamel which is crystalline, which inhibits the detection of anatase crystals, because the size of crystals is ~ 50 nm and crystallites could be dispersed on the surface or developed into enamel pores.

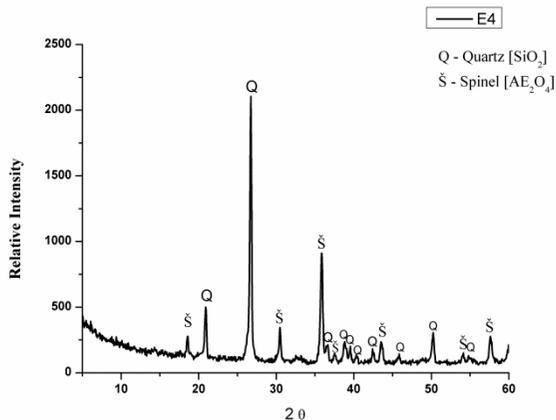


Figure 17. XRD patterns of enamel E4 with sol-gel coating T8S2. In turn, investigating the enamel with sol-gel coating by Raman spectroscopy, the presence of anatase was observed (Fig. 18.). The peaks at 143 , 198 , 397 , 517 and 650 cm^{-1} correspond to the anatase crystalline phase [11], while peaks at 465 and 700 cm^{-1} correspond to SiO_2 .

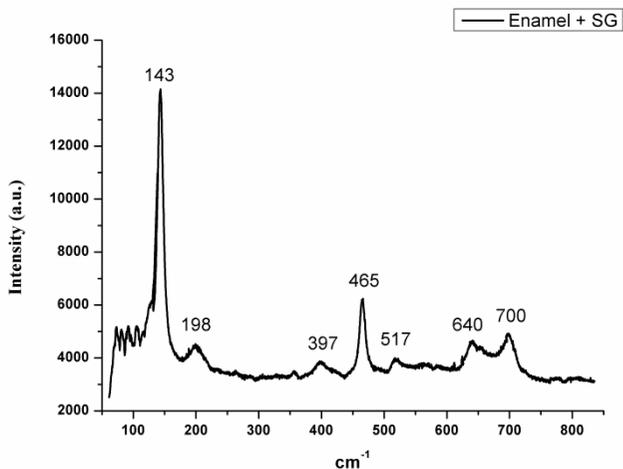


Figure 18. Raman spectra of enamel with T8S2 sol-gel coating.

4.5.1. Optical properties

After the deposition of sol-gel coating onto enamels, the light reflectance of samples was measured (Table 5). Obtained results show that sol-gel coatings slightly increase the light reflectance in 300-2500 nm wavelength range for all enamels. Most changes have been observed in the case of enamel E1, for which an initial reflectance was 29,96%, but after the sol-gel coating deposition – 31,84%. While, the smallest changes have been observed in the case of enamel E4, for which an initial reflectance was 7,01% while after deposition - 7,03%.

Table 5

Light reflection of enamels with sol-gel coating

Sample	E1	E1+SG	E2	E2+SG	E3	E3+SG	E4	E4+SG
300-2500 nm	29,96%	31,84%	30,68%	31,18%	29,7%	29,95%	7,01%	7,03%

To conclude about the spectral selectivity of enamels light reflection from 0,3 to 20 μm was measured (Fig. 19). As can be seen from the results, all enamels with sol-gel coating have quite high light reflectance in the infrared spectral region, which negatively affects the usability of material as possible CSP material, because it will have a high thermal emissivity.

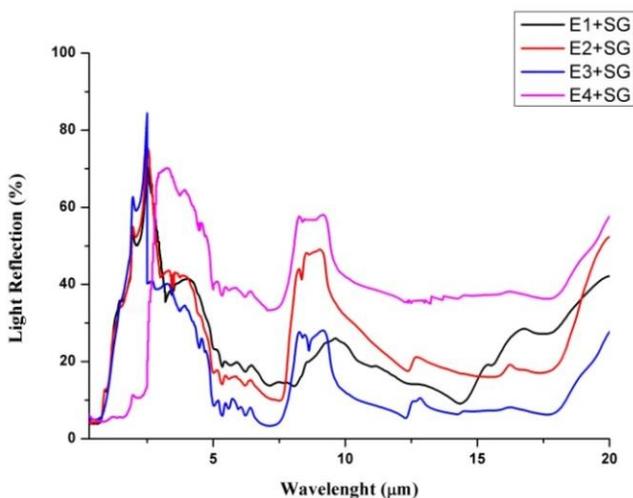


Figure 19. Light reflectance of enamels coated with T8S2 sol-gel coatings.

Using reflectance spectra the thermal emission of material was calculated, which results are summarized in Table 6. Results in the table show that thermal emission increases with increasing operation temperature. The lowest emission has enamel E4, which has the best light reflection, whereas the highest emission has enamel E1, which has lowest reflection. The lowest emission, the higher the efficiency of the collector, since absorbs solar heat not emitting it into the environment.

Table 6

Enamel emission at different temperatures

Enamel	ε (20°C)	ε (100°C)	ε (300°C)	ε (500°C)	ε (600°C)
E1	0,39	0,41	0,44	0,47	0,49
E2	0,35	0,37	0,41	0,45	0,47
E3	0,27	0,28	0,30	0,33	0,35
E4	0,18	0,19	0,21	0,23	0,25

The efficiency and selectivity of CSP material determines the ratio between the light absorption and emission, if the ratio is less than 1 then coating is non-selective, while if the ratio is greater than or equal to one, coating is selective or moderate selective. Table 7 summarizes the data of enamel selectivity.

Table 7

Results of enamel selectivity calculations

Enamel	α – absorption (%)	ε – emission (600°C)	α/ε
E1	0,68	0,49	1,39
E2	0,68	0,47	1,46
E3	0,70	0,35	2
E4	0,93	0,25	3,71

4.5.2. Photocatalytic activity

To get an idea of possible changes in photocatalytic activity the photocatalytic activity was determined both for sol-gel coatings deposited onto glass slides and enamels. Deposited coatings onto glass slides. Obtained results of photocatalytic activity (Fig. 20.) show that the photocatalytic activity slightly decreased of sol-gel coated enamel E4. Coating, which deposited onto enamel E4 produced 82% photocatalytic activity, while coating on glas slide - 88%. Observed difference in photocatalytic activity can be explained by anatase partice size onto the surface of coatings.

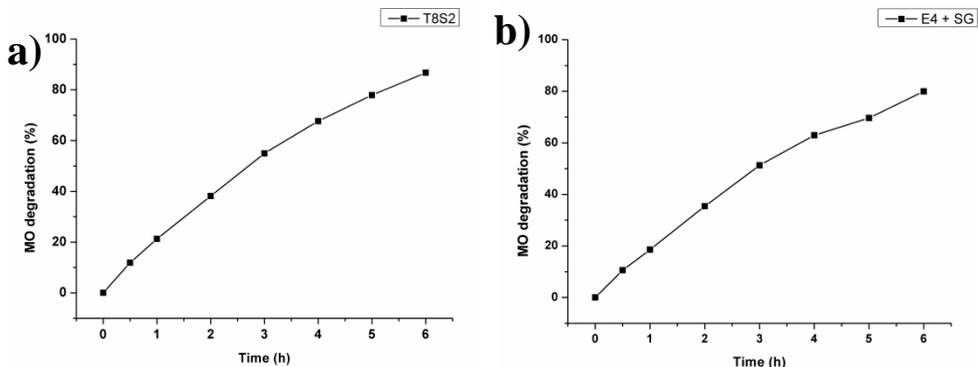


Figure 20. Photocatalytic activity of T8S2 sol-gel coatings on various substrates: a) glass slide with sol-gel coating b) enamel E4 with sol-gel coating.

4.5.3. Microhardness

Microhardness of enamels with sol-gel coatings was measured, because materials have potential application in CSP, which are located in the environment, so it is important to know the ability of material to resist physical influence (scratching). Microhardness of materials was determined by Vickers method and results are summarized in Table 8. As can be seen from the table, sol-gel coatings does not improve microgardness of enamel, which can be explained with the small thickness of sol-gel coating.

Table 8

Microhardness of enamels and enamels with sol-gel coating

Sample	E1	E1 SG	E2	E2SG	E3	E3SG	E4	E4SG
Microhardness (GPa)	2,13	2,19	2,82	2,81	2,62	2,59	2,75	2,76

4.5.4. Chemical resistance

Chemical resistance was measured for enamels and enamels with sol-gel coatings. Chemical resistance was tested against alkaline environment according to ISO 28706-4:2008. Test results are shown in Fig. 21. As shown sol-gel coating improves chemical resistance of enamel by 5-7%. It was found that enamel E2 is chemically most durable. Increased chemical resistance of enamel E2 is due to increased amount of amorphous

phase, in which crystalline formations are evenly dispersed. In addition, it is known from literature data aegerine crystals developed in enamel E2 have increased chemical resistance [12].

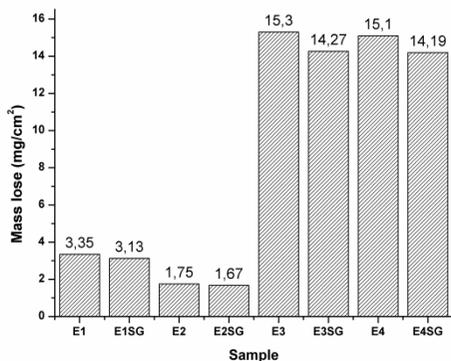


Figure 21. The results of chemical durability of enamels.

4.5.5 Porosity

The porosity was measured of most prospective enamels E3 and E4 which were uncoated and coated with sol-gel coatings. The results obtained (Fig. 22.) shows that coatings reduce the total porosity of enamel surface. This can be explained by the fact that sol-gel coating partially completed the largest pores and hence the smaller pores are detectable in the range of 0,1 to 0,01 μm .

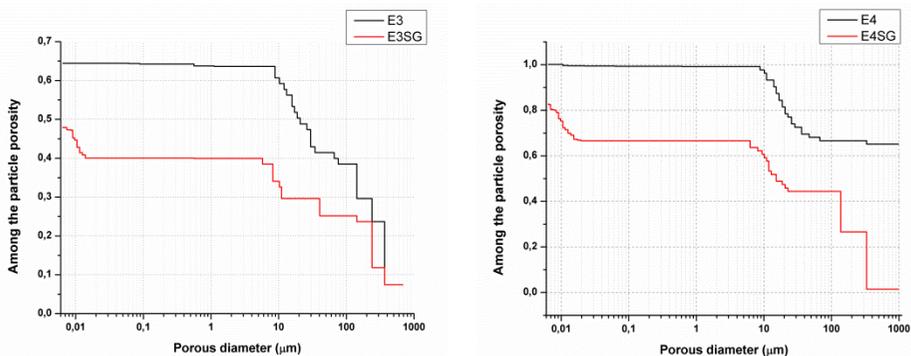


Figure 22. Porosity of enamels E3 and E4 with and without sol-gel coatings

4.6 Thermal resistance

As a major objective of this work the development of enamel with sol-gel coating with operating temperature above 600° C has been raised. To determine the thermal resistance of enamels and enamels with sol-gel coating, samples were placed in furnace at 600°C at atmospheric conditions, and the samples had to endure at least 3000 hours. After 3000 h coatings were characterized by light reflectance and XRD measurements. New crystalline phase formation even after heat treatment during 1000 h have been identified performing tests of enamels E1, E2 and E3. New crystalline phase - aegerine was formed and the reduction of crystalline phase peaks of iron chromium oxide (pigment) was detected in enamels, suggesting that the Fe³⁺ ions started intensively participate in the formation of aegerine crystalline phase. It was also found that the enamel E1 without sol-gel coating withstood only 2000 h without losing adhesion to the substrate, while sol-gel coated E1 enamel withstood 3000 h. XRD pattern of enamel E4 after thermal test is shown in Fig. 23. As can be seen, only two crystalline phases quartz and spinel are present in enamel is, which does not changes during heat treatment, but the intensity of peaks increases.

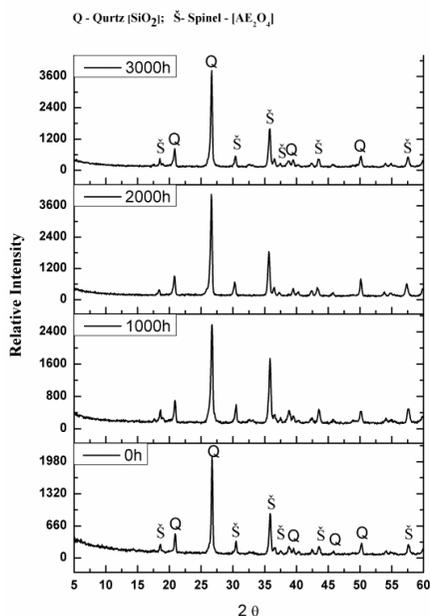


Figure 23. XRD patterns of enamel E4 with sol-gel coating.

After thermal resistance test the light reflectance spectra were measured of in the range of 300-2500 nm, results are summarized in Table 9. Obtained results show that sol-gel coating helps to retain spectral properties of enamel, – the light reflectance of enamel E4 increases only by 0,5% comparing to data obtained before and after thermal treatment test.

Table 9
Light reflection of enamels with sol-gel coating after thermal test

Sample	E1	E1SG	E2	E2SG	E3	E3SG	E4	E4SG
Before test	29,96%	31,84%	30,68%	31,18%	29,7%	29,95%	7,01%	7,03%
After test	38,53%	36,33%	37,16%	31,64%	33,06%	32,72%	8,56%	7,54%

Photocatalytic activity test of the best enamels E3 SG and E4 SG with sol-gel coating after thermal treatment test was determined. And in both cases, it was observed that photocatalytic activity significantly decreases, which could be explained by the increase of crystal size onto the surface of coatings. From the Fig. 24 it can be seen that activity decreases from 82% to 40%.

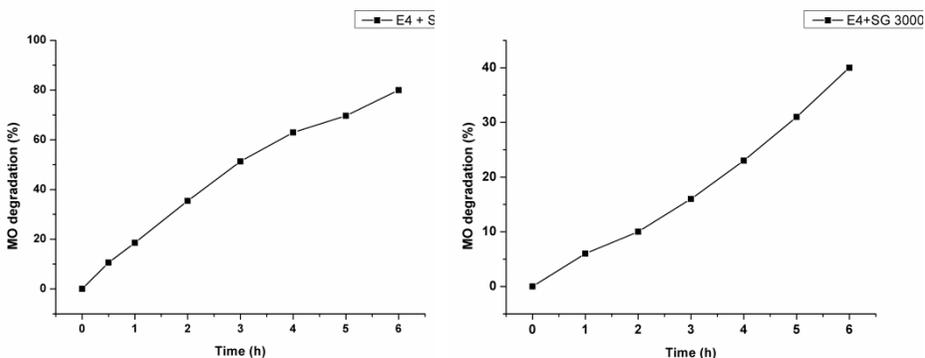


Figure 24. Photocatalytic activity of enamel E4 with sol-gel coating before and after thermal resistance test

Enamel microhardnesses of enamels and enamels with sol-gel coating after the thermal test was measured. Results are summarized in the Table 10. As can be seen from previous results enamel E1 failed 3000 h test and it was not possible to determine its microhardness, in all other samples

microhardness was determined. As can be seen the performance of enamel with sol-gel coating was better than of uncoated enamels. It means that the sol-gel coating protects enamel from thermal oxidation and from the rapid decline of mechanical properties.

Table 10

Microhadness of enamels and enamels with sol-gel coating after thermal test

Sample	E1	E1SG	E2	E2SG	E3	E3SG	E4	E4SG
Before test (GPa)	2,13	2,19	2,82	2,81	2,62	2,59	2,75	2,76
After test (GPa)	-	1,09	2,04	2,35	2,53	2,58	2,71	2,74

Chemical durability results of enamels are shown in Table 11. Similarly to the microhardness, chemical durability was measured after thermal resistance test. As can be seen from results, the sol-gel coating for enamel E2 increases chemical durability by ~ 30% while for enamels E3 and E4 the sol-gel coating only slightly, by ~ 6%improves the durability .

Table 11

Chemical durability of enamels and enamels with sol-gel coating after thermal resistance test

Sample	E1	E1SG	E2	E2SG	E3	E3SG	E4	E4SG
Before test, (g)	3,35	3,13	1,75	1,67	15,3	14,27	15,1	14,19
After test, (g)	-	44,73	12,62	8,96	15,52	14,52	15,23	14,38

CONCLUSIONS

1. Thin sol-gel coatings of various systems (single and two component) were synthesized during that work by dip-coating method onto enamel surface, providing an increased chemical resistance against NaOH solution, saved microhardness and high light transmission (> 90%).
2. Applying compositions of sol-gel binary system TiO₂-SiO₂, where TiO₂ molar concentration did not exceeded 80 mol% it is possible to stabilize anatase crystalline phase in sol-gel coatings at temperatures higher than 500° C.
3. Choosing appropriate regimes of coating sintering and drying, as well as introducing Fe₂O₃ in the composition of sols

nanostructured coatings on enamel surface with high photocatalytic activity were obtained. Synthesized thin films characterized with photocatalytic activity in the UV and visible light spectrum. Coatings were able to degrade 88% MO during 6 hours in UV light, and 45% of MO in visible light range.

4. Approximate porosity of enamels with applied sol-gel coating could be evaluated using Hg porosimeter. It is estimated that the porosity of borosilicate enamel modified by sol-gel coating was reduced by 25-30% in comparison with enamel without sol-gel coating. Reduced porosity of enamel improved the thermal and chemical durability of enamel.
5. Using traditional enamelling method with mill additives and pigment it is possible to obtain enamel coating onto chromium nickel steel alloy (Stainless steel 321A) with light reflection in the range from 300 to 2000 nm not exceeding ~ 7%.
6. The material with low light reflectance, high photocatalytic activity and good chemical and thermal resistance at 600°C that could be potentially applied in CSP collectors was developed.

PUBLICATIONS

Patents

1. European patent application EP 2881440 A1 "Double-layer coating on alloy steel", G.Mežinskis, I.Pavlovskā, L.Bidermanis, **K.Malniēks** 10.06.2015
2. European patent application EP 2 871 168 A1 "Mass of silicate enamel coating on steel", G.Mežinskis, L. Bidermanis, I.Pavlovskā, A. Cimmers, J.Liepīns, **K.Malniēks**. J. Gabrusenoks 13.05.2015
3. LR Patent Nr. 14646. "Mass of crystalline silicate enamel coating on steel" L.Bīdermanis, J.Liepīņš, G.Mežinskis, I.Pavlovskā, A.Cimmers, L.Lindīņa, **K.Malniēks**. 20.05.2013

Publications

1. Gundars Mezinskis, Ilona Pavlovskā, **Kaspars Malnieks**, Laimonis Bidermanis, Andris Cimmers, Pavels Onufrijevs „Long-term stability at high temperature of sol-gel coated enamel for steel” *Progress in Organic coatings* (submitted) 15.11.2015 (SCOPUS)
2. **K.Malnieks**, G.Mezinskis, I.Pavlovskā, A.Pludons „Effect of different dip-coating techniques on TiO₂ thin film properties” *Ceramic International* (submitted) 20.04.2015 (SCOPUS)
3. **K.Malnieks**, I.Pavlovskā, G.Mezinskis, L. Bidermanis, J.Liepins, A. Pludons” Black enamel for concentrated solar-power receivers” *Ceramic International*, 40, 13321-13327, 2014 DOI: 10.1016/j.ceramint.2014.05.046
4. Ilona Pavlovskā, **Kaspars Malnieks**, Gundars Mezinskis, Laimonis Bidermanis, Margarita Karpe” Hard TiO₂-SiO₂ sol-gel coatings for enamel against chemical corrosion” *Surface & Coating Technology*, 258, 206-210, 2014 <http://dx.doi.org/10.1016/j.surfcoat.2014.09.027> (SCOPUS)
5. **K.Malnieks**, G.Mezinskis, I.Pavlovskā, L.Bidermanis, A.Pludons „Optical, photocatalytic and structural properties of TiO₂ – SiO₂ sol-gel coatings on high content SiO₂ enamel surface”, *Materials Science (MEDŽIAGOTYRA)*, 21(1), 100-104, 2014 DOI: <http://dx.doi.org/10.5755/j01.ms.21.1.5188> (SCOPUS)

Conference abstracts

1. **K.Malnieks**, G.Mezinskis, I.Pavlovskā, L.Bidermanis „Enamel as high temperature solar light receiver”. *BaltSilica 2014*, 01.06-03.06.2014. Poznan, Poland
2. **K.Malnieks**, G.Mezinskis, I.Pavlovskā, L.Bidermanis” Antireflective and photocatalytic sol-gel coating on enamel” *Riga Technical University 54th International Scientific Conference*, Riga, Latvia, 14.10-16.10.2013.
3. **K.Malnieks**, I.Pavlovskā „Emaljas seguma nepārtrauktības nodrošināšana, pielietojot sol-gēla pārklājumu” 52. *RTU Studentu zinātniskā un tehniskā konference*, Rīga, Latvija, 29.04.2011.
4. **K.Malnieks**, G.Mezinskis, L.Bidermanis, I.Pavlovskā, J.Liepins, A.Pludons. „Porosity reduction of borsilicate glass enamel by TiO₂-SiO₂ sol-gel coating” *BaltSilica 2011: 5th Baltic Conference of Silicate Materials*, Riga, Latvia, 23.05.-25.05.2011.

CONFERENCES

1. **K.Malniēks**, G.Meziņskis, I.Pavlovska „Different dip-coating technique impact on TiO₂ thin film properties”, 7th International Conference on Silicate Materials "BaltSilica 2016, Kaunas, Lithuania, May 26-27, 2016
2. **K.Malniēks**, G.Meziņskis, I.Pavlovska, L.Bidermanis “Black enamel as high temperature solar light receiver material” Riga Technical University 56 International Scientific Conference, Riga, Latvia, October 14-16, 2015
3. **K.Malniēks**, G.Meziņskis, I.Pavlovska, L.Bidermanis „Enamel as high temperature solar light receiver” 6th Baltic conference on silicate materials 2015, Poznan, Poland, June 1-3, 2014
4. **K.Malniēks**, G.Meziņskis, I.Pavlovska, L.Bidermanis “Antireflective and photocatalytic sol-gel coating on enamel” Riga Technical University 54 International Scientific Conference, Riga, Latvia, October 14-16, 2013
5. **K.Malniēks**, I.Pavlovska „Emaljas seguma nepārtrauktības nodrošināšana, pielietojot sol-gēla pārklājumus” 52. RTU studentu zinātniskā un tehniskā konference 2011, Riga, Latvija, Aprīlis 29, 2011.
6. **K.Malniēks**, G.Meziņskis, L.Bidermanis, I.Pavlovska, J.Liepins, A.Pludons “Porosity reduction of borosilicate glass enamel by TiO₂-SiO₂ sol-gel coatings.” 5th Baltic conference on silicate materials 2011, Riga, Latvia, May 23-25, 2011
7. **K.Malniēks**, G.Meziņskis, I.Pavlovska “TiO₂-SiO₂ sola-gēla pārklājumi emaljas virsmas porainības samazināšanai” Riga Technical University 51 International Scientific Conference, Riga, Latvia, October 11-15, 2010
8. **K.Malniēks**, I.Pavlovska „Sola-gēla pārklājumi emaljas virsmas porainības samazināšanai.” 50. RTU studentu zinātniskā un tehniskā konference, Rīga, Latvija, Aprīlis 30, 2009.

REFERENCES

1. M.A.Villegas. Chemical and microstructural characterization of sol-gel coatings in the ZrO₂ – SiO₂ system. *Thin Solid Films.*, **2001**, 382(1-2), 124–132.
2. Thin Films / internets http://en.wikipedia.org/wiki/Thin_film#External_links

3. G.Xu, Z.Zheng, Y.Wu, N.Feng. Effect of silica on the microstructure and photocatalytic properties of titania. *Ceram. Int.*, **2007**, doi: 10.1016/j.ceramint.2007.09.008.
4. M.Garcia-Heras, J.M.Rincon, M.Romero, M.A.Villegas. Intendation properties of ZrO₂-SiO₂ coatings on glass substrates. *Mater. Res. Bull.*, **2003**, 38, 1635-1644.
5. M. De Lucia, C.P. Mengoni. Analysis of Total-Energy Solutions for a Shopping Centre Part 2: Solar Assisted Cooling Solutions, OTTI-Solar AIR Conditioning, 9781617822285, Vol. 1, OTTI-Solar AIR Conditioning - Tarragona – SPAIN, **2007**, 226-232
6. C. Cinelli, M. De Lucia, P. Giovannetti, C.P. Mengoni, S. Toccafondi. Medium temperature PTC collector: experimental analysis and performance, ASME, Vol. ASME-ATI-UIT Thermal and Environmental Issues in Energy Systems, n. 5, Month, ASME - Sorrento IT, **2010**, 1-5
7. A. Brunotte, M. Lazarov, and R. Sizmann. Calorimetric measurements of the total hemispherical emittance of selective surfaces at high temperatures, A. Hugot-Le Goff, C. G. Granqvist, C. M. Lampert, *eds.*, *SPIE*, 1727, 1992, 149
8. W.Bogaert, C.Lampert,. Materials for photothermal solar energy conversion, *J. of Mat.Sci.*, **1983**, 2847-2875.
9. N. Xu, Z. Shi, Y. Fan, J. Dong, J. Shi, M.Z. Hu, Effects of Particle Size of TiO₂ on Photocatalytic Degradation of Methylene Blue in Aqueous Suspensions, *Ind.Eng.Chem. Res.* **38**, **1999**, 373-379
10. S.F. Resende, E.H.M. Nunes, M. Houmard, W.L. Vasconcelos. Simple sol-gel process to obtain silica-coated anatase particles with enhanced TiO₂-SiO₂ interfacial area” *Journal of Colloid and Interface Science*, 433, **2014**, 211-217
11. M. J. Ščepanović, M. Grujić-Brojčin, Z. D. Dohčević-Mitrović, Z. V. Popović,. Characterization of Anatase TiO₂ Nanopowder by Variable-Temperature Raman Spectroscopy, *Science of Sintering*, 41, **2009**, 67-73
12. A. Goel, E.R. Shaaban, J.B. Oliveira, M.A. Sá, M.J. Pascual, J.M.F. Ferreira. Sintering behavior devitrification kinetics of iron containing clinopyroxene based magnetic glass-ceramics., *Solid State Ionics* 186, **2011**, 59-68.