KOROZIJSKA ZAŠTITA SAMOORGANIZIRAJUĆIM FILMOVIMA ORGANSKIH KISELINA

CORROSION PROTECTION BY SELF-ASSEMBLED FILMS OF ORGANIC ACIDS

Ekatarina Kristan Mioč[1], **Vedrana Katić**[1], **Helena Otmačić Ćurković**[1]

[1] Faculty of Chemical Engineering and Technology, University of Zagreb, Savska cesta 16, 10000 Zagreb, Croatia

Abstract

Self-assembled monolayers (SAMs) of long-chain organic compounds have found their application in many fields such as sensors, electronic devices, lubrication as well as in corrosion protection. Most of the studies on SAMs application in corrosion protection are conducted by using alkanethioles SAMs on copper and silver. However, if metallic substrate is covered by an oxide layer corrosion protection by SAMs of alkanethioles is much weaker compared to those on non-oxidized metallic substrates. Thus, SAMs of long-chain organic acids that can bind strongly to oxidized metallic surfaces are much better choice for many commonly used metals and alloys. This work investigates the possibility of corrosion protection of stainless steel in chloride media by self-assembled mono- and multilayers of long-chain phosphonic acids. Various parameters of SAM preparation procedure determine if well-ordered and protective film will form, among others temperature, solution exposure time, surface roughness, solvent, etc. In this work the influence of solvent, organic acid concentration and drying time and temperature on its protective properties are examined. Based on the results obtained by electrochemical measurements and surface analysis, the optimal conditions for formation of protective organic film have been determined.

Keywords: *Corrosion protection, stainless steel, self-assembled monolayers.*

Corresponding author: Helena Otmačić Ćurković, helena.otmacic@fkit.hr

1. INTRODUCTION

Self-assembled monolayers (SAMs) of long-chain organic compounds have found their application in many fields such as sensors, electronic devices, lubrication as well as in corrosion protection. Compared to other methods for surface modification, SAMs have many advantages – only a small amount of organic compounds is needed to cover the metal surface, they can be easily prepared and they form through the chemisorption of molecules on the solid substrate. The most commonly studied SAM systems are thiols on the non-oxidized metal surfaces and silanes on oxide surfaces. However, the major disadvantages of these two systems are their oxidation in time or instability in aqueous and biological media [1–3]. The promising replacement for thiols and silanes are long-chain organic acids, especially phosphonate acids since they are relatively stable and can be attached to a wide range of oxide surfaces [4–9]. It is important to emphasize that many studies have been conducted on pure metals while studies on alloys are much scarcer.

Moreover, although stainless steel 316L is widely used as a biomaterial, very few papers on SAMs on stainless steel have been reported in the literature. Also, most of the studies on phosphonic acids SAMs are based on their physical properties, characterization of SAM structure and initial corrosion protection [4–7,9], but there are far less studies that focus on efficiency and durability of corrosion protection [10–12], which is very important for materials in the practical use.

The stability of self-assembled monolayers (SAMs) of functionalized alkyl phosphonic acids formed on stainless steel [12,13] was studied under physiological conditions. It was discovered that the SAMs was stable up to 1 to 7 days but suffered substantially from desorption afterwards. Several research groups have noted that thermally treating the films (100 – 120 °C) before using them for further studies [13–15] enhances the stability of films but these studies lack visual evidence.

The structure, stability and number of defects in the final monolayer formed on metal surface strongly depend on the nature of the solvent used. The solvent parameters, such as dielectric constant and interaction ability, are important factors that affect the quality of monolayer. According to literature [16] the higher the dielectric constant of solvent from which the monolayer is assembled, the lower surface density of molecules, the greater number of defects, and the less robust SAMs will be formed. But on the other hand, it is important that solvent must not complex with a surface. [16]

The purpose of this study was to examine how various parameters of SAM preparation procedure, i.e. drying time and temperature, concentration in various solvents and choice solvents with different dielectric constants, affect the quality of monolayer assembled on metal surface and the long-term corrosion protection.

1. EXPERIMENTAL

2.1. Materials and sample preparation

In order to prepare working electrodes, stainless steel rod, AISI 316L, was cut-out in 0.5 cm thick samples and on their back side a copper wire was soldered. At the end they were embedded into epoxy resin and the exposed surface of working electrode was 1.13 cm^2. The electrodes were, prior to all surface treatment, abraded with emery paper grade 80, 240, 400, 800, 1200 and 2500, degreased with ethanol in ultrasonic bath and rinsed with re-distilled water. Octadecylphosphonic acid was obtained from Sigma-

Aldrich Corp. USA and ethanol (EtOH) and tetrahydrofuran (THF) were obtained from Lach-ner d.o.o. Croatia.

The SAM formation was carried out by the following procedure: oxide formation, 24 h at 80◦C, followed by acid adsorption from EtOH, THF or water solution of ODPA, 20 h at 40 °C [17], and final drying step, 5 h at 80 °C or 1 h at 110 °C. The use of THF, as a solvent besides ethanol and water, was motivated by studies that show that better quality layers form in solvents with lower dielectric constant. [18] However, since the epoxy resin can degrade in a prolonged contact with THF, a Teflon holder was used instead of epoxy resin for electrochemical measurements of samples with THF deposited SAMs. Firstly, the optimal preparation procedure (influence of temperature and drying time) was investigated with ODPA ethanol solution at 10^{-2} M concentration, and after optimizing the preparation procedure, experiments were continued with investigation of ODPA concentration in various solvents: 10^{-2}, 10^{-3} and 10^{-4} M in ethanol and THF, and 10^{-3} and 10^{-4} M in water.

2.2. Electrochemical investigations

The electrochemical investigations were conducted in a three electrode cell, in a 3 % NaCl solution. A platinum foil and saturated calomel electrode were used as the counter and reference electrode, respectively. All potentials in the text are referenced against saturated calomel electrode (SCE). Prior to electrochemical measurements the electrodes were immersed in the test solution for 1 hour to stabilize at the open circuit potential (E_{oc}). The polarization measurements were performed at the wide (± 150 mV vs. E_{oc}) potential range, with a potential scan rate of 0.166 mV s^{-1}. Corrosion current density (j_{corr}) was determined by Tafel extrapolation method. The electrochemical impedance spectroscopy (EIS) was performed at E_{oc} in the frequency range of 100 kHz to 10 mHz with a 10 mV_{rms} amplitude. The electrochemical measurements were performed using a Bio-Logic SP-300 potentiostat.

2.3. Contact angle measurements

Contact angle measurements were performed in order to obtain information about the properties of the surface of the monolayer as well as the packing density. The water contact angle measurements (CA) on bare and treated samples were performed using a goniometer DataPhysics Contact Angle System OCA 20, with a drop of 2 μL deionized water under the ambient atmospheric conditions.

2. RESULTS

2.1. Preparation procedure optimization

Protective films of ODPA were formed on the metal oxide surface of SS316L using dip-coating method described above. In order to determine the optimal SAM preparation procedure studies were performed in 0.01 M ODPA ethanol solution. In Fig. 1 are presented results obtained for non-treated and ODPA treated samples with different parameters of the drying step (on 80 °C for 5 h and on 110 °C for 1 h).

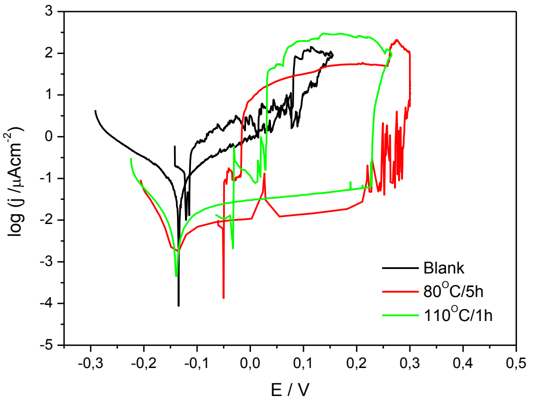


Fig. 1: Polarization curves for ODPA/EtOH samples dried at different temperatures

Tab. 1: Corrosion parameters determined by Tafel extrapolation method from polarization curves given in Fig. 1.

Sample	E_{corr} (mV)	j_{corr} (μA/cm^2)	β_a (mV/dek)	$-\beta_c$ (mV/dek)	CR (mm/god)	E_{BD} (V)	$j_{pass, 0 V}$ (μA/cm^2)	E_{RP} (V)
Blank	-134,4	0,127	147,3	160,3	0,001324	0,15	0,501	-0,11
80°C/5h	-142,5	0,005	305,9	56,9	0,000052	0,30	0,010	-0,05
110°C/1h	-139,2	0,008	154,5	71,1	0,000083	0,24	0,032	-0,03

From polarization curves given in Figure 1 and corrosion parameters determined by Tafel extrapolation from polarization curves given in Table 1, it is visible that both ODPA treated samples exhibit lower current densities compared to blank SS316L sample. As it can be seen, for treated samples both anodic and cathodic current densities were reduced. The best results were obtained when drying step were conducted at 80 °C for 5 h with lower current densities, especially anodic current densities, and higher inhibition efficiency.

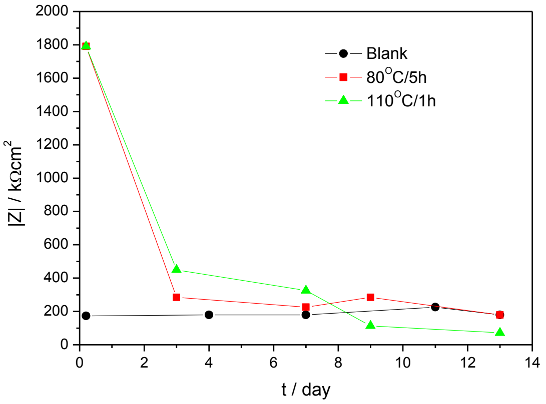


Fig. 2: Impedance modulus dependence on time of exposure to chloride medium

For application of SAMs in a corrosion protection it is not sufficient to determine only the initial protection level but also to verify if the protection remains satisfactory in time. For that reason electrochemical impedance spectroscopy measurements were conducted over longer period of time. The impedance modulus values determined from the EIS measurements at 0,01 Hz are given in Figure 2.

It can be observed that for the first day polarization resistance of both samples was higher than for bare non-treated sample, but after the third day values of polarization resistance decreased. From these results it can be concluded that higher drying temperature is not increasing the corrosion inhibition efficiency of formed ODPA film.

The influence of time of ODPA adsorption from ethanol solution was also examined as an important parameter of SAM formation procedure. Impedance modulus evolution in time of exposure to corrosive medium is given in Figure 3. Initially sample with the film formed during longer time showed better protective properties, but after 11 days protection of both samples has diminished.

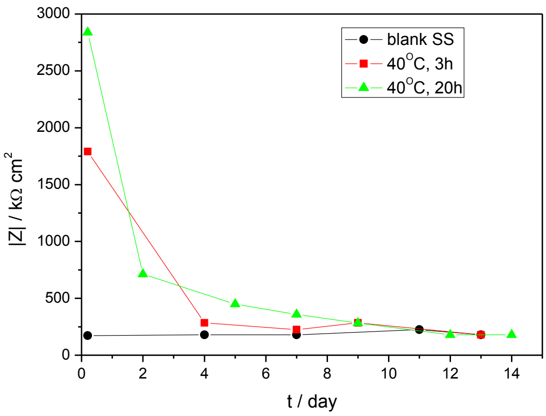


Fig. 3: Impedance modulus dependence on time of exposure to chloride medium: samples prepared by adsorption at 40°C/3h and40°C/20h

Therefore, the influence of optimal ODPA concentration in solvents with different dielectric constants was investigated on samples which were dried at 80 °C for 5 h and adsorption step was conducted during 20h.

2.2. The influence of ODPA concentration in different solvents

2.2.1. Ethanol

From polarization curves given in Figure 4 and corrosion parameters given in Table 2, it is visible that for all treated samples both anodic and cathodic current densities were reduced compared to blank SS316L sample. Decrease of cathodic current densities can be related to formation of barrier organic film that slows down the diffusion of oxygen and thus the rate of its reduction. Treated samples also shown much lower anodic current densities, more positive values of the potential for breakdown (E_{BD}) of passivity and the repassivation potential (E_{RP}) compared with non-treated SS316L sample. Therefore, it can be concluded that all treated sample have shown efficient corrosion protection. However, as it can be seen from graphs and table above, the best results were obtained with the highest concentration.

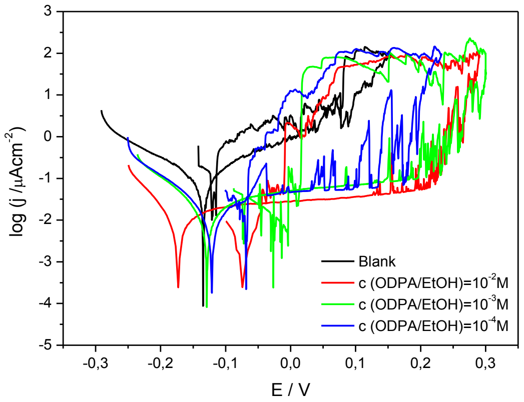


Fig. 4: Polarization curves for samples treated with different concentrations of ODPA/EtOH

Tab. 2: Corrosion parameters determined by Tafel extrapolation method from polarization curves given in Fig. 4.

Sample	E_{corr} (mV)	j_{corr} (μA/cm^2)	β_a (mV/dek)	$-\beta_c$ (mV/dek)	CR (mm/god)	E_{BD} (V)	$j_{pass,\,0\,V}$ (μA/cm^2)	E_{RP} (V)
Blank	-134,4	0,127	147,3	160,3	0,001324	0,15	0,501	-0,11
10^{-2} M	-173,3	0,009	216,9	62,0	0,000094	0,28	0,025	-0,01
10^{-3} M	-130,4	0,021	305,1	96,9	0,000219	0,30	0,050	-0,02
10^{-4} M	-120,0	0,015	184,4	87,6	0,000156	0,23	0,032	-0,07

The polarization resistance values as a function of immersion time in the sodium solution determined for samples treated with different concentration of ODPA are given in Figure 5. It can be seen that the highest polarization resistance value initially was obtained for the SAM formed in the highest concentration of ODPA molecules in ethanol. Unfortunately, values decrease in time and after few days are similar to non-treated sample.

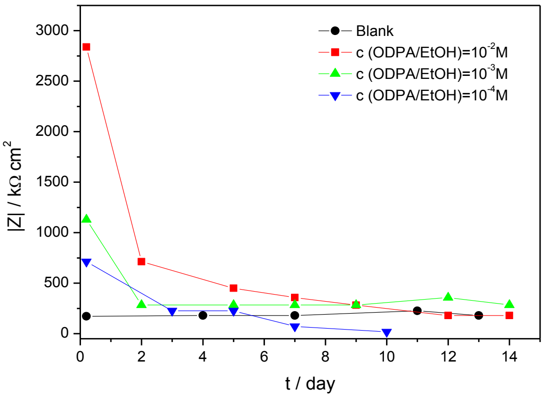


Fig. 5: Impedance modulus dependence on time of exposure to chloride medium

3.2.2. Tetrahydrofuran

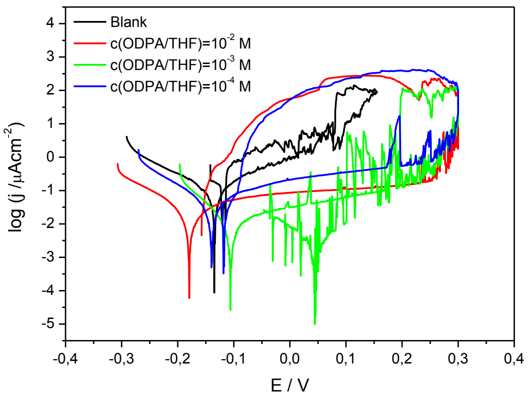


Fig. 6: Polarization curves for ODPA/THF treated samples

Tab. 3: Corrosion parameters determined by Tafel extrapolation method from polarization curves given in Fig. 6.

Sample	E_{corr} (mV)	j_{corr} (µA/cm^2)	β_a (mV/dek)	$-\beta_c$ (mV/dek)	CR (mm/god)	E_{BD} (V)	$j_{pass,\ 0\ V}$ (µA/cm^2)	E_{RP} (V)
Blank	-134,4	0,127	147,3	160,3	0,001324	0,15	0,501	-0,11
10^{-2} M	-179,2	0,026	278,7	115,7	0,000271	0,30	0,063	-0,16
10^{-3} M	-105,4	0,011	207,5	70,9	0,000115	0,30	0,032	0,17
10^{-4} M	-139,1	0,040	163,2	105,4	0,000417	0,30	0,251	-0,09

Polarization curves recorded after one hour exposure to 3 % NaCl solution (Figure 6) show that when THF was used as a solvent both anodic and cathodic densities decreased. The highest corrosion rate reduction has been achieved when sample was treated with *c* (ODPA/THF) = 10^{-3} M. It has more positive values of the repassivation potential (Table 3) compared with the other samples, and this indicates reduction of localized corrosion tendency.

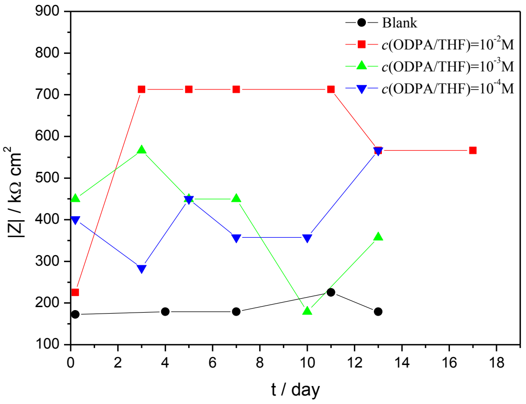


Fig. 7: Impedance modulus dependence on time of exposure to chloride medium

It can be observed in Figure 7. that all ODPA films formed in THF solution show polarization resistance higher than of the bare non-treated sample, and compared with films formed in ODPA/EtOH solution, films formed in THF show better corrosion resistance and stability in time of exposure to chloride medium. Although initially the highest corrosion protection shows *c* (ODPA/THF) = 10^{-3} M sample, in time of exposure to corrosive medium probably because of molecules rearrangement the highest corrosion stability has film formed in higher concentration of ODPA.

3.2.3. Water

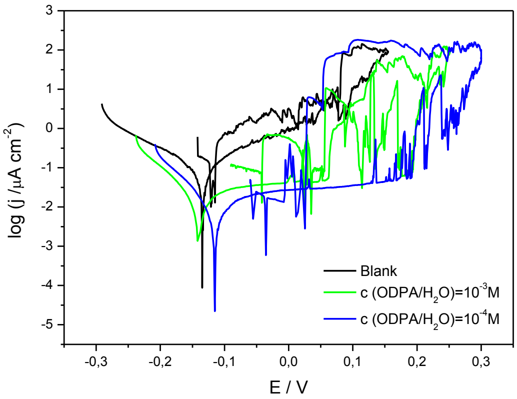


Fig. 8: Polarization curves for ODPA/H_2O treated samples

Tab. 4: Corrosion parameters determined by Tafel extrapolation method from polarization curves given in Fig. 8.

Sample	E_{corr} (mV)	j_{corr} (μA/cm^2)	β_a (mV/dek)	-β_c (mV/dek)	CR (mm/god)	E_{BD} (V)	$j_{pass,\ 0\ V}$ (μA/cm^2)	E_{RP} (V)
Blank	-134,4	0,127	147,3	160,3	0,001324	0,15	0,501	-0,11
10^{-3} M	-140,6	0,018	267,2	75,6	0,000188	0,24	0,032	0,08
10^{-4} M	-115,0	0,010	207,8	68,1	0,000104	0,29	0,020	0,03

From polarization curves given in Figure 8 and corrosion parameters given in Table 4, it is visible that for all treated samples both anodic and cathodic current densities were reduced compared to blank sample. When layer was formed by adsorption in 10^{-3} M ODPA/H_2O solution, there was a shift of corrosion potential in cathodic direction, and that can be related to formation of barrier organic film that slows down the diffusion of oxygen and thus the rate of its reduction. ODPA film formed in lower concentration solutions has shown lower anodic current density and lower passive current density, and a shift of corrosion potential in anodic direction, which shows strong anodic corrosion reaction inhibition.

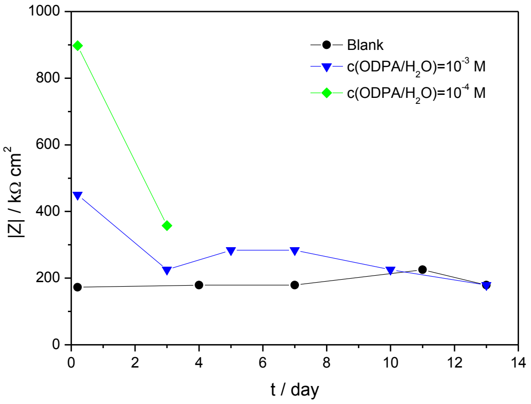
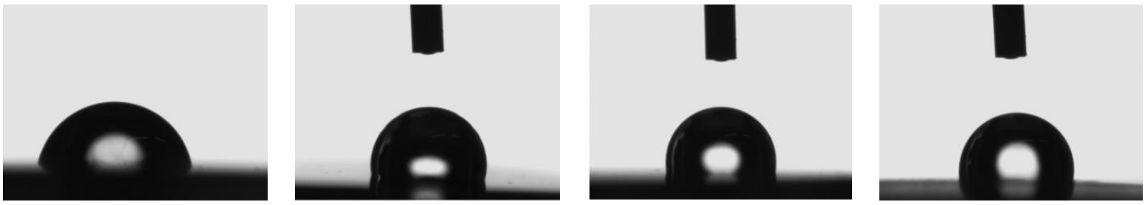


Fig. 9: Polarization resistance dependence on time of exposure to chloride medium

From Figure 9. it can be seen that, although ODPA film formed in lower concentration showed initially higher polarization resistance value, this value decreases in time. It can be assumed that due to low solubility of ODPA in water micelle-like structures adsorbed on metal surface, which can be easily desorbed from the surface in corrosive medium.

2.3. Contact angle measurements

Surface wettability has been shown to be useful tool for estimating the monolayer quality. Densely packed and well-ordered monolayers predominantly expose methyl groups at the surface and decrease the surface wettability. However, loosely packed monolayers expose both methyl and methylen groups at the surface which results in increased wettability. [19]



Blank ODPA/EtOH ODPA/THF ODPA/H$_2$O

Fig. 9: Images of drop of water on ODPA films formed in different solvents

Tab. 5: Contact angles of a drop of water on ODPA films formed in different solvents

Sample	Contact angle / °
Blank	72,0 ± 1,0
ODPA/EtOH	104,0 ± 0,8
ODPA/THF	102,8 ± 0,7
ODPA/H$_2$O	100,4 ± 1,6

Contact angle measurements (Figure 9. and Table 5.) show that all surfaces treated with octadecylphosphonic acid have hydrophobic properties, i.e. contact angle above 100°, and non-treated sample has hydrophilic properties. Different values of contact angles indicate that formed layers have various structures and homogeneity. It can be emphasize that the highest value was obtained when ethanol was used as a solvent.

3. CONCLUSION

In this work the influence of parameters procedure of preparation and possibility of corrosion protection of stainless steel 316L by self-assembled layers of octadecylphosphonic acid was examined. Results of electrochemical investigation show that in order to obtain the efficient protection the time of adsorption was important for stability of protective films. The best results were obtained with the highest examined concentration of ODPA. All modificated steel surfaces had hydrophobic properties.

Results obtained in this work indicate that choice of solvent has significant impact on the initial and long-term corrosion protection. The lowest protection was observed when water was used as a solvent. Excellent initial corrosion protection was observed when ethanol was used as a solvent but it diminishes rapidly in time. Samples prepared in THF solution showed the best stability and long-term corrosion protection.

Acknowledgement:
The research leading to these results has received funding from Croatian Science Foundation under grant agreement 9.01/253.

REFERENCES

[1] Flynn, N. T., Tran, T. N. T., Cima, M. J., Langer, R., Long-Term Stability of Self-Assembled Monolayers in Biological Media, Langmuir, 19, pp. 10909–10915, (2003).

[2] Sung, I. H., Kim, D. E., Surface Damage Characteristics of Self-Assembled Monolayers of Alkanethiols on Metal Surfaces, Tribol. Lett., 17, pp. 835–844, (2004).

[3] Willey, T. M., Vance, A. L., Buuren, T., Bostedt, C., Terminello, L. J., Fadley, C. S., Rapid degradation of alkanethiol-based self-assembled monolayers on gold in ambient laboratory conditions, Surf. Sci., 576, pp. 188–196, (2005).

[4] Hauffman, T., Hubin, A., Terryn, H., Study of the self-assembling of n-octylphosphonic acid layers on aluminum oxide from ethanolic solutions, Proceedings, Surface and Interface Analysis, pp. 1435-1440, (2013).

[5] Silverman, B. M., Wieghaus, K. A., Schwartz, J., Comparative Properties of Siloxane vs Phosphonate Monolayers on A Key Titanium Alloy, Langmuir, 21, pp. 225–228, (2005).

[6] Quiñones, R., Raman, A., Gawalt, E. S., Functionalization of nickel oxide using alkylphosphonic acid self-assembled monolayers, Thin Solid Films, 516, pp. 8774–8781, (2008).

[7] Raman, A., Dubey, M., Gouzman, I., Gawalt, E. S., Formation of self-assembled monolayers of alkylphosphonic acid on the native oxide surface of SS316L, Langmuir, 22, pp. 6469–6472, (2006).

[8] Branch, B., Dubey, M., Anderson, A. S., Artyushkova, K., Baldwin, J. K., Petsev, D., Dattelbaum, A. M., Investigating phosphonate monolayer stability on ALD oxide surfaces, Appl. Surf. Sci., 288, pp. 98–108, (2014).

[9] Dubey, M., Weidner, T., Gamble, L. J., Castner, D. G., Structure and order of phosphonic acid-based self-assembled monolayers on Si(100), Langmuir, 26, pp. 14747–14754, (2010).

[10] Cichomski, M., Kośla, K., Grobelny, J., Kozłowski, W., Szmaja, W., Tribological and stability investigations of alkylphosphonic acids on alumina surface, Appl. Surf. Sci., 273, pp. 570–577, (2013).

[11] Bhure, R., Abdel-Fattah, T. M., Bonner, C., Hall, F., Mahapatro, A., Stability of phosphonic self assembled monolayers (SAMs) on cobalt chromium (Co-Cr) alloy under oxidative conditions, Appl. Surf. Sci., 257, pp. 5605–5612, (2011).

[12] Kaufmann, C. R., Mani, G., Marton, D., Johnson, D. M., Agrawal, C. M., Long-term stability of self-assembled monolayers on 316L stainless steel, Biomed. Mater., 5, pp. 25008, (2010).

[13] Lim, M. S., Smiley, K. J., Gawalt, E. S., Thermally treated octadecylphosphonic acid thin film grown on SS316L and its stability in aqueous environment, ACS Symp. Ser., 1070, pp. 193–204, (2011).

[14] Gao, W., Dickinson, L., Grozinger, C., Morin, F. G., Reven, L., Self-Assembled Monolayers of Alkylphosphonic Acids on Metal Oxides, Langmuir, 12, pp. 6429-6435, (1996).

[15] Gawalt, E. S., Avaltroni, M. J., Koch, N., Schwartz, J., Self-Assembly and Bonding of Alkanephosphonic Acids on the Native Oxide Surface of Titanium, Langmuir, 17, pp. 5736–5738, (2001).

[16] Chen, X., Luais, E., Darwish, N., Ciampi, S., Thordarson, P., Gooding, J. J., Studies on the Effect of Solvents on Self-Assembled Monolayers Formed from Organophosphonic Acids on Indium Tin Oxide, Langmuir, 28, pp. 9487-9495, (2012).

[17] Hajdari Gretić, Z., Kristan Mioč, E., Čadež, V., Šegota, S., Otmačić Ćurković, H., Hosseinpour, S., The Influence of Thickness of Stearic Acid Self-Assembled Film on Its Protective Properties, J. Electrochem. Soc., 163, pp. C937–C944, (2016).

[18] De Pauli, M., Prado, M. D. C., Matos, M. J. S., Fontes, G. N., Perez, C. A., Mazzoni, M. S. C., Neves, B. R. A., Malachias, A., Thermal stability and ordering study of long- and short-alkyl chain phosphonic acid multilayers, Langmuir, 28, pp. 15124–15133, (2012).

[19] Raman, A., Gawalt, E. S., Self-assembled monolayers of alkanoic acids on the native oxide surface of SS316L by solution deposition, Langmuir, 23, pp. 2284–2288, (2007).