Processing and Application of Ceramics 9 [2] (2015) 81–89
DOI: 10.2298/PAC1502081K

Sol-gel derived coatings for the conservation of steel

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Received 1 April 2015; Received in revised form 8 June 2015; Accepted 18 June 2015

Abstract

In this paper, sol-gel processing route has been applied and investigated for the conservation of steel. Nanosilica coatings on steel surface have been prepared using tetraethylorthosilicate (TEOS) as a starting material. The methyl-modified silica sols were obtained by mixing of 3 mas.% SiO_2 sol solution with hexamethyldisilozane (HMDS). The surface of steel was coated by dip-coating technique. In order to compare the characteristics of coatings, the steel substrates were also coated with commercial polymers Paraloid B67, Cosmolloid H80 and Antik Patina. The surface morphology changes of the uncoated and coated specimens before and after photochemical ageing were investigated by scanning electron microscopy and atomic force microscopy. The structure of the prepared coatings was also investigated by FTIR spectroscopy. The hydrophobicity of surfaces was evaluated by contact angle measurements. Potentiodynamic measurements were obtained in order to compare corrosion parameters of the coatings.

Keywords: *sol-gel method, steel, silica coatings, conservation*

I. Introduction

The science of conservation chemistry has been widely developed in the last decades. Various new materials were suggested and applied in conservation and restoration of metals. An increased resistance of metals and alloys to corrosion is generally obtained by the formation of a protective layer isolating the substrate from the surrounding oxidant atmosphere [1]. Diverse protective coatings, such as nitrides, carbides, silicides or transition metal oxides, have been already deposited on steel [2,3]. Mild steel is inexpensive and widely used structural material in several applications [4]. It has, however, limited service life unless effective measures are taken to improve its corrosion and wear resistance properties [5–10]. Ceramic based coatings are increasingly used for range of industrial applications to provide wear and erosion resistance and corrosion protection [11,12].

Sol-gel coatings are good alternatives to toxic treatments for corrosion protection of metallic cultural heritage objects. Their main action is to act as physical barriers against aggressive environments [13]. The first studies were focused on the formation of pure inorganic sol-gel films [14,15]. These studies have shown that after the deposition films have to be treated in high temperature. Moreover, it was difficult to obtain thick coatings without cracks. In 2004, Ono *et al.* [16] showed that adding organic compound to the matrix eliminates cracking. Moreover, heat treatment can be lowered after the sol deposition and films are more flexible as well as denser. Hence, hybrid sol-gel coatings have been widely developed. Van Ooij *et al.* [17] and Wang *et al.* [18] reviewed recent advances made with this technology. Besides that, methyl-modified sol-gel coatings for the conservation of copper has already been described recently [19].

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Namely, the use of this technique for coating metals was essentially aimed at testing the capability of sol-gel coatings to improve the oxidation and corrosion resistance of the substrate [20–22]. However, other examples of applications have been reported. Sol-gel technique is widely used in conservation of glass, stone and other materials. The use of this technique in conservation of metals is not widely investigated yet. The most important advantages of the sol-gel method for this kind of application are: lower processing temperature, no limits in the size or shape of the substrates, the possibility of work in a continuous process in normal atmospheric conditions, homogeneous and constant thickness, high control of the film composition and low costs in the equipment and process in general [23].

The aim of this work was to investigate and apply sol-gel technique for the preparation of protective coatings on steel substrate. Hybrid silica coatings have been prepared using dip-coating technique. Methyl groups were used as silica modifiers in order to increase protective and hydrophobic properties of the coating. Polymeric and bitumen coatings – Paraloid B67, Cosmolloid H80 and Antik Patina that are used in conservation of metals were also deposited on the surface of steel in order to compare their properties with the prepared silica coatings. All the measurements were performed before and after the photochemical ageing.

II. Experimental

2.1. Preparation of sols and solutions

Tetraethylorthosilicate (TEOS, Fluka, ≥98%) was used as a precursor to prepare colloidal silica sols. Ethanol (EtOH) and NH_4OH were used as a solvent and catalyst, respectively. Precursor silica sol, with the concentration of 3 mas.% SiO_2, was obtained by alkaline catalysis as previous study [19] revealed that this method is more perspective in metal conservation rather than acidic one. The molar ratio of components TEOS:NH_4OH:H_2O:EtOH during alkaline catalysis was 1:0.2:2.97:34.72. In order to complete the hydrolysis, the obtained SiO_2 sol was aged for 19 days at 25 °C and used in further coating and modification process. The modification of colloidal nano-silica was performed by adding 8 mas.% of hexamethyldisilozane (HMDS; Sigma Aldrich, ≥98%) to the prepared alkaline sol. The alkaline and methyl-modified sols were used to obtain the coatings on steel substrate. Polymeric and bitumen coatings – Paraloid B67, Cosmolloid H80 and Antik Patina (Kremer Pigmente GmbH & Co) that are used in conservation of metals were also deposited on the surface of steel. The solvents and concentrations have been chosen considering the conservators' recipes: 1 mas.% Paraloid B67 in acetone, 6 mas.% Cosmolloid H80 in toluene and 10 mas.% Antik Patina in white spirit. Solutions were aged at a room temperature (25 °C) for 2 days.

2.2. Preparation of films

Steel substrates (1 × 1.5 cm, 0.5 mm thick steel foil, Alfa Aesar) were treated mechanically with aluminium oxide paper and then washed with ethanol. Different protective coatings were attained on the steel plates by the dip-coating process. The dip-coating was performed by immersing the pre-treated steel substrate into the sol or solution (polymeric, bitumen, etc.) by the speed of 85 mm/min. The specimen retained in the sol-gel solution for 20 s and followed by withdrawal of the pretreated steel substrate from the solution by the speed of 40 mm/min. The process was performed in a constant temperature and atmosphere in a laminar box.

2.3. Characterization

The coatings were characterized by contact angle measurements, atomic force microscopy (AFM), scanning electron microscopy with energy dispersive X-ray analysis (SEM/EDX), infrared spectroscopy (FTIR) and electrochemical measurements. The contact angle was measured with Contact Angle Meter KSV Instruments CAM – 100. The static water contact angles were measured at ten different positions for each sample, and the average value was admitted as the contact angle. Characterization of the coatings was also performed using FTIR (Perkin Elmer Frontier FT-IR with ATR module) spectroscopy. Optical subsystem was used to capture the profile of pure liquid on a solid substrate. AFM (Bioscope II, Veeco) was used to obtain topographic images and investigate the morphology of the samples. Hitachi TM3000 scanning electron microscope with INCA energy dispersive spectrometer (Oxford Instruments) was used to obtain SEM images and perform EDX analysis. Electrochemical measurements were performed using a standard three-electrode electrochemical cell with auxiliary Pt electrode and silver/silver chloride reference electrode. Standard electrochemical potential of AgCl is $E^{\circ}_{\mathrm{Ag/AgCl}} = 0.197$ V. Electrochemical parameters, j_{corr} – corrosion current, E_{corr} – corrosion potential, R_p – corrosion rate resistance, were obtained. The potential at which the current reaches its maximum, the current in the region where there is a little change in current with potential and the potential at which the current begins to increase again are used in materials selection of design of corrosion control systems. Reversing the scan to determine the potential at which the reverse scan crosses the forward scan provides information on the tendency of the metal to pit.

2.4. Artificial ageing

All obtained coatings were exposed to artificial ageing in a photochemical reactor. Philips luminescence lamps PL–9W110 of 40 W that emit in the range of 350–400 nm were used in a photochemical reactor. The specimens were placed 0.5 cm above the lamps. The temperature in the reactor was 40 °C and relative humidity 17%. The samples had been aged for 28 days.

Table 1. The contact angles determined on uncoated steel specimen and differently coated steel surfaces before and after photochemical ageing

No.	Coating conditions	Contact angle [°]		
		before ageing	after ageing for 14 days	after ageing for 28 days
1	3 mas.% SiO_2	65.2(3)	43.3(4)	35.2(1)
2	10 mas.% Antik Patina	96.5(2)	67.5(7)	63.5(4)
3	Uncoated steel specimen	88.9(8)	84.6(5)	79.1(3)
4	1 mas.% Paraloid B67	90.8(1)	83.9(2)	83.9(2)
5	6 mas.% Cosmolloid H80	128.5(3)	104.7(6)	103.8(9)
6	Alkaline 3 mas.% SiO_2 with HMDS	150.7(7)	142.9(8)	151.2(5)

III. Results and discussion

3.1. Contact angle measurements

Coated samples were aged in a photochemical reactor under the conditions described in the Experimental part. Periodical photo-fixation and contact angle measurements have been performed. Considering the visual observations, steel substrates were not affected rapidly. However, the coatings became more opaque. In order to ascertain the influence of artificial ageing on the hydrophobicity, the results of contact angle measurements have been summarized in Table 1. As can be seen, the contact angle value of the uncoated steel substrate is 88.9° and decreased up to 84.6° after the 14 days of photochemical ageing. Moreover, the value slightly decreases up to 79.1° during the next 14 days. The materials widely used in conservation of metals and other cultural heritage objects were also used for the preparation of coatings on the surface of steel in order to compare the characteristics of coatings obtained from nano-silica. Apparently, the coatings that are obtained from Cosmolloid H80 and Antik Patina are hydrophobic as the contact angle values before the photochemical ageing were 128.5° and 96.8°, respectively, i.e. higher than 90°. However, the contact angle value of coating with Paraloid B67 was lower (90.8°) and can not be attributed to the hydrophobic ones. The contact angle values of these coatings decreased only in the first stage of photochemical ageing (14 days) as extending the period of artificial ageing only slightly affected the hydrophobic properties of these coatings.

The least value of contact angle (65.2°) was determined for the unmodified nano-silica coating obtained from alkaline SiO_2 sol. This might be associated with existence of hydrophilic –OH groups on the surface of nano-silica [24]. Obviously, the results demonstrated that contact angle value of the SiO_2 coatings on steel decreased gradually until 35.2° during the photochemical ageing. Surprisingly, the contact angle value significantly increased after modification of nano-silica surface with the HMDS and reached 150.7°. The coating is also affected by photochemical ageing and the value of contact angle decreased to 142.9° after 14 days. The HMDS modified coating on steel surface remained hydrophobic even after photochemical ageing for 28 days. The images of water drop on the steel surfaces coated with nano-silica modified with HMDS are shown in Fig. 1.

The results of contact angle measurements revealed that all coatings were differently affected by photochemical ageing. Namely, the SiO_2, Paraloid B67 and Antik Patina coatings on steel substrate are not suitable for its conservation since hydrophilic coatings are formed after the photochemical ageing. The coating, obtained from Cosmolloid H80 was hydrophobic before (128.5°) and after the photochemical ageing (103.8°). However, the highest contact angle value before and after the photochemical ageing was stated in the SiO_2 coating modified with HMDS (~150°). However, for the final conclusions more physico-chemical characterizations of surfaces were performed and are presented in the next subsections.

3.2. Atomic force microscopy

Three-dimensional topographic AFM images of the uncoated and conservated steel specimens are presented in Figs. 2 and 3. Obviously, the surfaces of the uncoated and coated specimens with polymers are rough with well pronounced scratches. However, these rapid scratches are related only to the surface of specimen

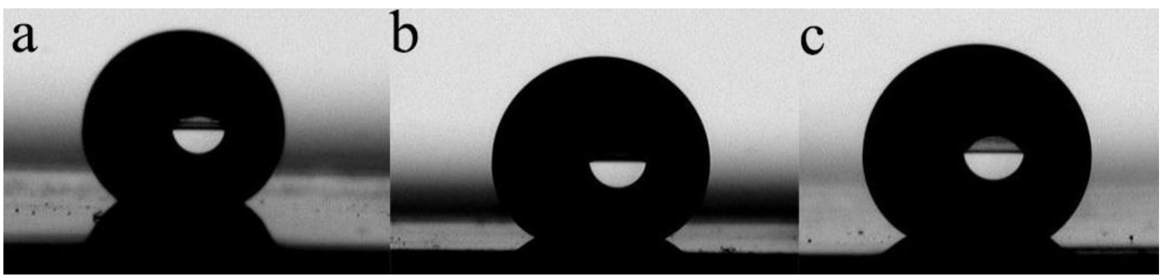

Figure 1. The images of water drop on steel surfaces coated with SiO_2 modified with HMDS: a) before photochemical ageing, b) after ageing for 14 days and c) for 28 days

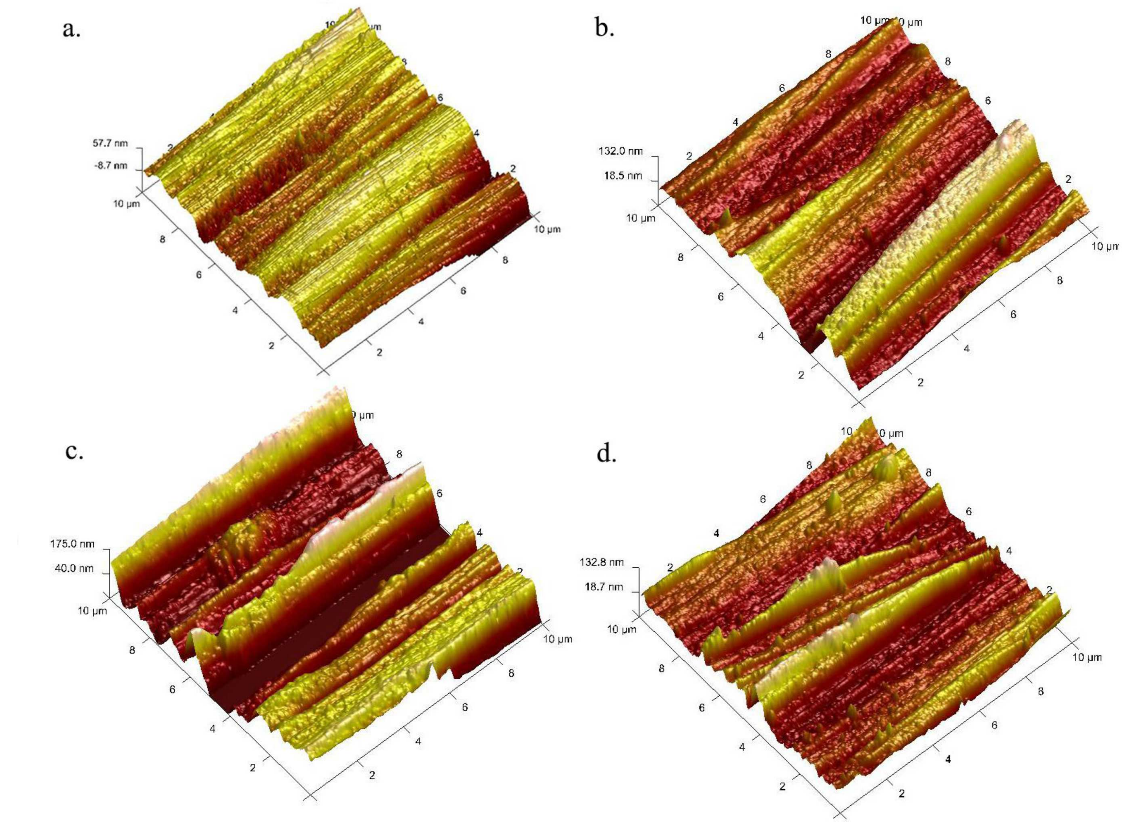

Figure 2. AFM images of: a) uncoated steel substrate and coated with b) Paraloid B67, c) Cosmolloid H80 and d) Antik Patina

which was affected during the cleaning process, i.e. polishing the steel substrates with aluminium oxide paper. However, the determined morphology of the nano-silica coatings modified with HMDS was different. Evidently, the obtained coatings are more even, the scratches of specimens are not visible. It is interesting to note, that photochemical ageing did not affect the roughness of the surfaces. Thus, according to the AFM measurements, it can be concluded that even coatings on the steel substrate could be obtained by dip-coating in the methyl-modified nano-silica gels. The roughness of the scratched surface is reduced to the minimum by applying this coating processing.

3.3. FTIR spectroscopy

The structure of the coatings was evaluated by FTIR spectroscopy. The spectra of the polymer coatings are not added due to widely investigated properties of polymer coatings in scientific articles [25–30].

FTIR spectra of the pure SiO_2 and SiO_2 modified with HMDS before the photochemical ageing are presented in Figs. 4a,c. Absorption bands due to vibrations of asymmetric Si–O (1082 cm^{-1}), Si–OH (961 cm^{-1}) and symmetric Si–O (793 cm^{-1}) are seen in the spectra. It can be stated that addition of HMDS decrease the intensity of wide and not intensive band at 3450–3400 cm^{-1} which indicates –OH group. Thus, a part of these groups

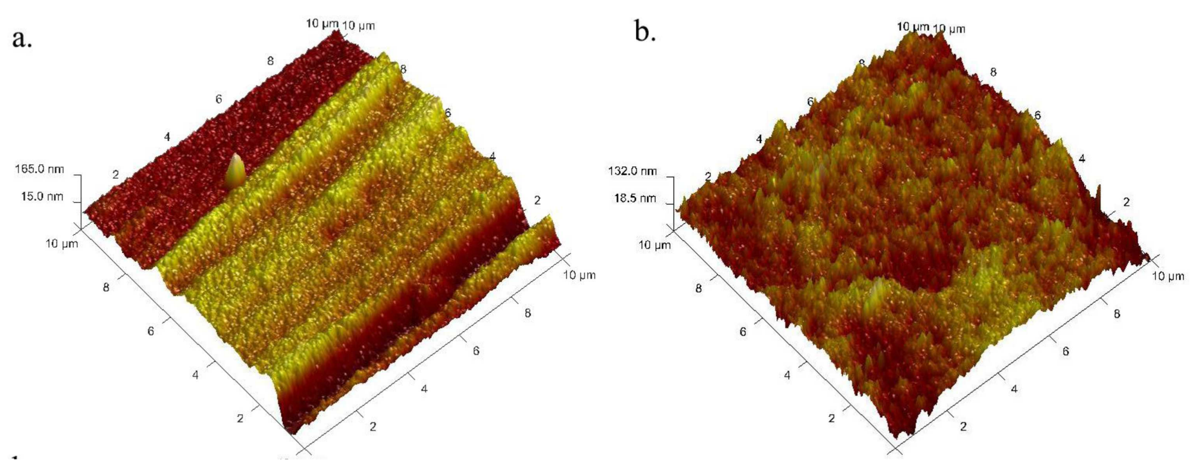

Figure 3. AFM images of steel substrate coated with: a) SiO_2 and b) SiO_2 modified with HMDS

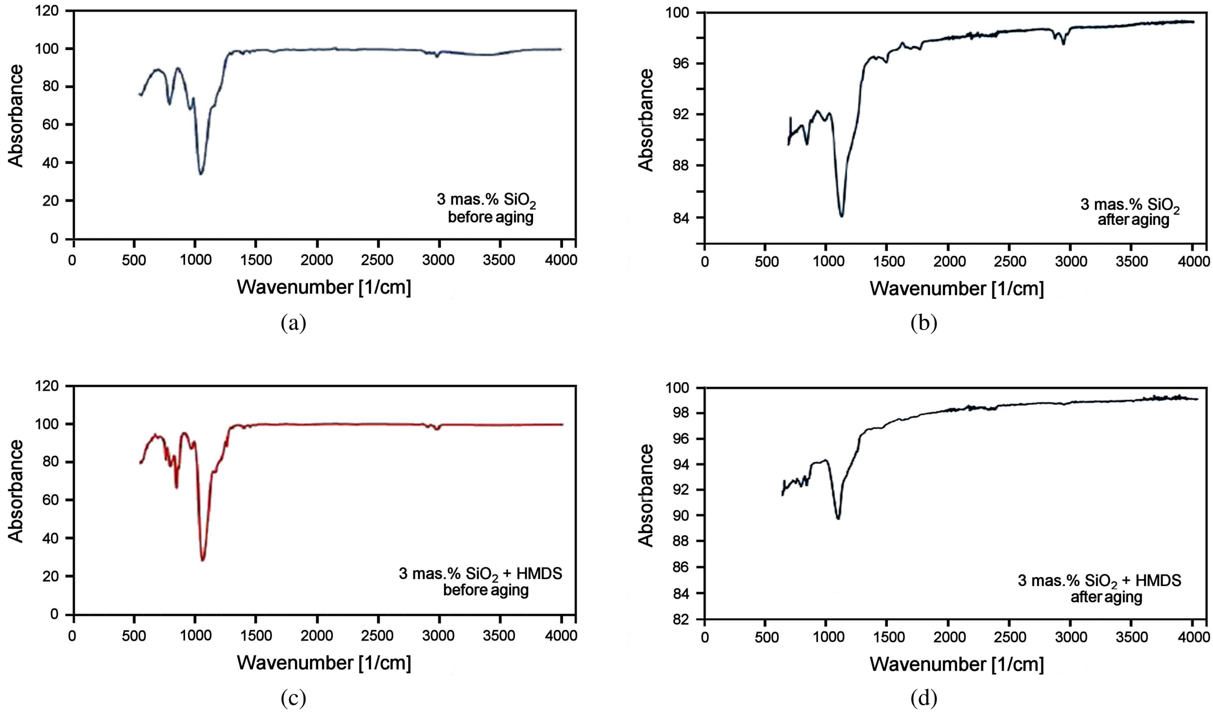

Figure 4. FTIR spectra of SiO_2 coatings before (a) and after (b) the photochemical ageing and SiO_2 modified with HMDS coatings before (c) and after (d) the photochemical ageing

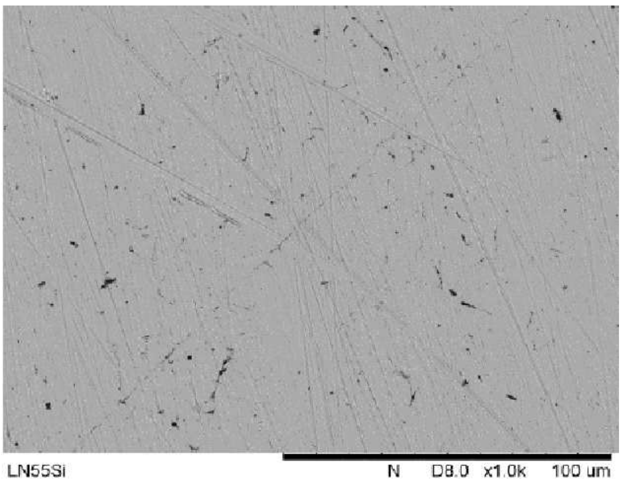

Figure 5. SEM micrograph of un-coated steel specimen

are changed by $OSi(Me)_3$ groups during the modification of SiO_2. Low intensity band at 2985 cm^{-1} is associated with vibrations of C–H bonds. In the pure SiO_2 coating, absorption bands of Si–O, C–H or O–H remain after the photochemical ageing (Fig. 4b). However, additional bands appear in the range of 1500 cm^{-1} to 1700 cm^{-1}. The exact origin of these bands is not known. However, the presence of these bands indicates the destruction process in the coating. On the other hand, FTIR spectrum of SiO_2 modified with HMDS remains unchanged after the photochemical ageing (Fig. 4d). Vibrations and intensities of Si–O (1089 cm^{-1} and 804 cm^{-1}), Si–OH (976 cm cm^{-1}) and C–H (2955 cm^{-1}, 1445 cm^{-1}) are observed. Thus, FTIR results indicate that the SiO_2 coating modified with HMDS is highly resistance to photochemical ageing.

3.4. Scanning electron microscopy

SEM analysis was used to investigate morphological features of the uncoated and differently coated steel surfaces before and after the photochemical ageing. It is clearly seen, that the surface of the uncoated steel substrate (Fig. 5) is composed of differently oriented lines and traces originated from the surface preparation and cleaning procedure. Some black spots could be also detected on the surface of the steel surface. Figure 6 presents the SEM images of the SiO_2 coating on the steel substrate prepared using alkaline conditions. Clearly, the steel surface before ageing is scratched, however, the traces are spread in a parallel manner. So, the coating gradually covers the scratched areas and partially repeats the roughness of the surface. No cracks or fractures are noticed during the morphological study of this specimen. Moreover, coating is very uniform even after the photochemical ageing (Fig. 6b). However, the morphology of the coating is slightly affected by the appearance of small dark spots on the surface.

SEM images of the steel substrates covered with the polymer coatings are shown in Fig. 7. Noticeably, the coatings, obtained from Cosmolloid H80 and Antik Patina before the photochemical ageing, are uniform oppositely to the coatings obtained from Paraloid B67 which were strongly cracked. After the photochemical ageing intensive dark spots appeared in the coatings obtained from Cosmolloid H80 and Antik Patina. However, the poor quality coatings obtained by dipping the

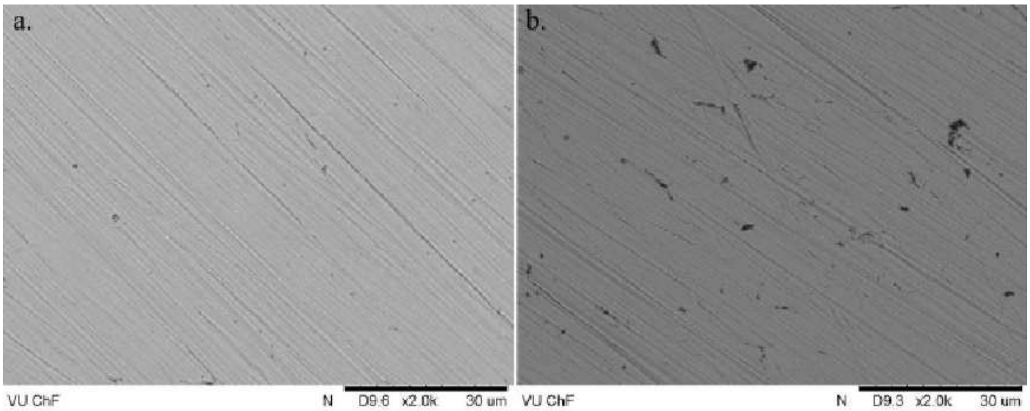

Figure 6. SEM micrographs of steel substrates coated with SiO_2 before (a) and after (b) photochemical ageing

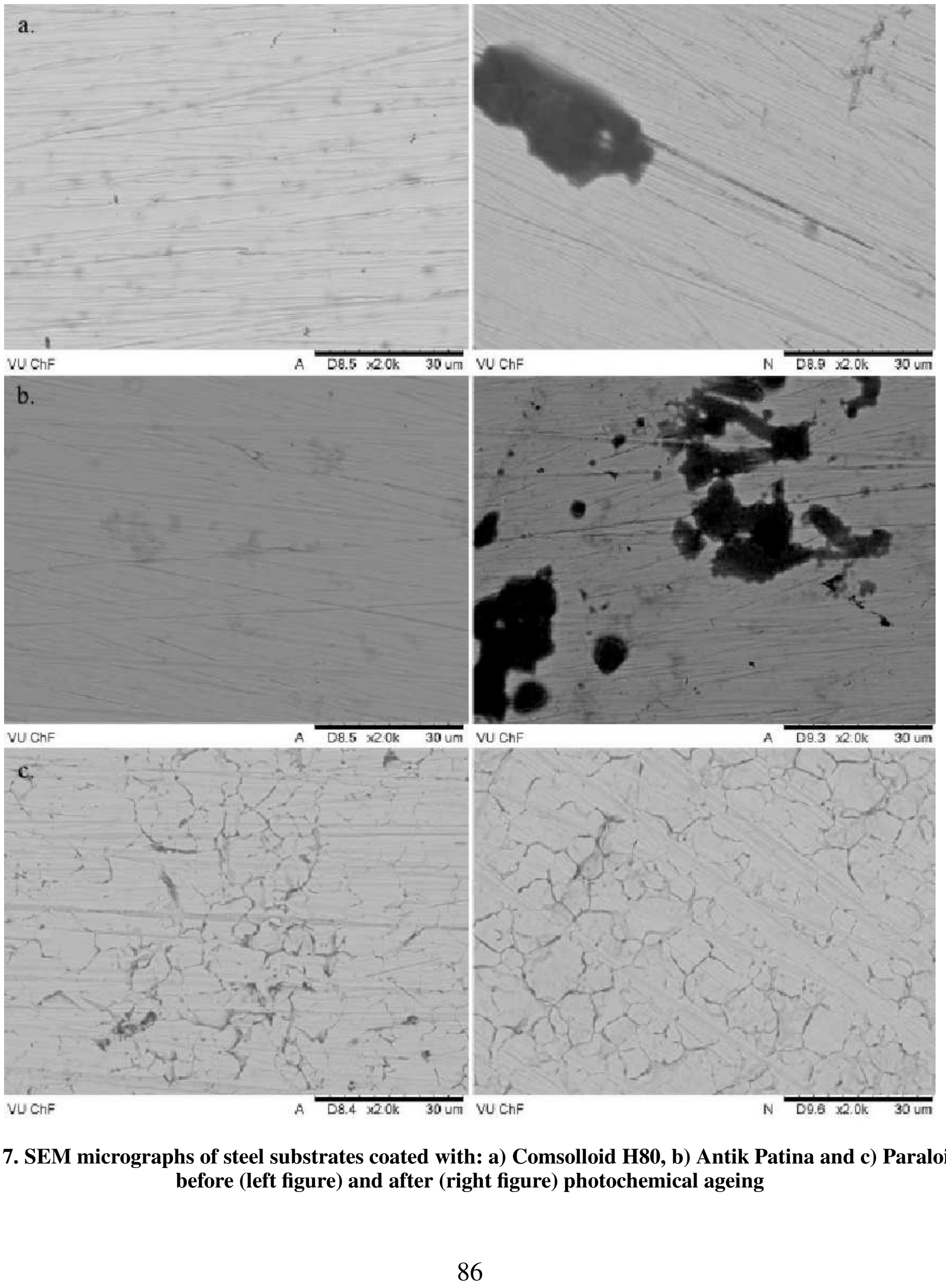

Figure 7. SEM micrographs of steel substrates coated with: a) Comsolloid H80, b) Antik Patina and c) Paraloid B67 before (left figure) and after (right figure) photochemical ageing

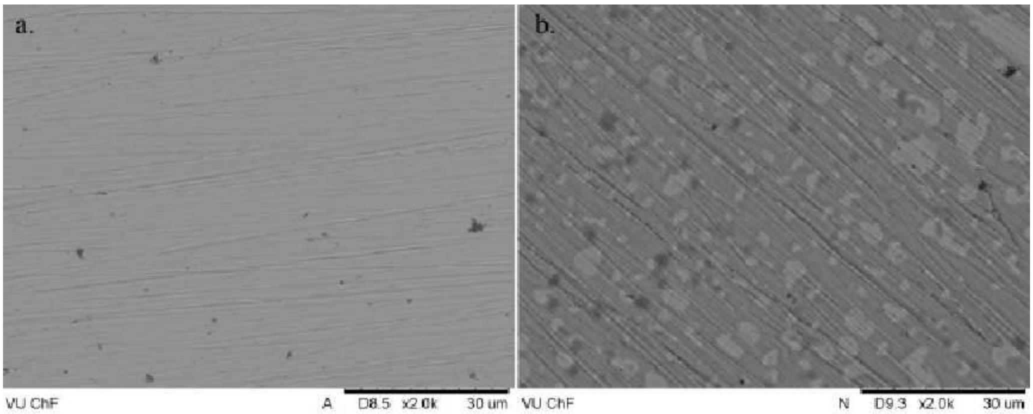

Figure 8. SEM micrographs of steel substrates coated with HMDS modified SiO_2: a) before and b) after photochemical ageing

steel substrate in the solution of Paraloid B67 remain almost without changes after the photochemical ageing.

The SEM micrographs of the SiO_2 coatings prepared using alkaline sol-gel conditions and modified with HMDS are shown in Fig. 8. The microstructure of this coating slightly differs from that without HMDS. It is noticed that the surface is smooth and even with some slightly visible horizontally parallel scratches. Moreover, the rare dark spots on the coating observed after the photochemical ageing are smaller. Besides, the specific network of light spots, having size of 1–5 µm, was formed on the surface of the coating. The origin of this phenomenon is not clear, but might be associated with better hydrophobic characteristics of the HMDS modified nano-silica coatings.

The EDX analysis of different areas of the samples was also performed. The interest was focused on distribution of concentration of carbon, nitrogen and silica in the coatings. The EDX analysis data confirmed the presence of main elements in the corresponding coatings. However, the results of EDX analysis were scattered and did not provide any additional information. Moreover, EDX method is not very accurate quantitative method for measuring lightweight atoms.

3.5. Potentiodynamic polarization measurements

Corrosion parameters of the uncoated specimen and coatings on steel substrate were evaluated by performing potentiodynamic polarization measurements. Polarization curves recorded on the alkaline SiO_2, SiO_2:HMDS and polymer coatings before the photochemical ageing are shown in Fig. 9. The calculated data of corrosion parameters before and after the photochemical ageing is presented in Table 2. As seen (Table 2 and Fig. 9), before the photochemical ageing the worst corrosion parameters are found for the uncoated steel specimen. Namely, the coated steel specimens are better protected from the environmental impact than the un-

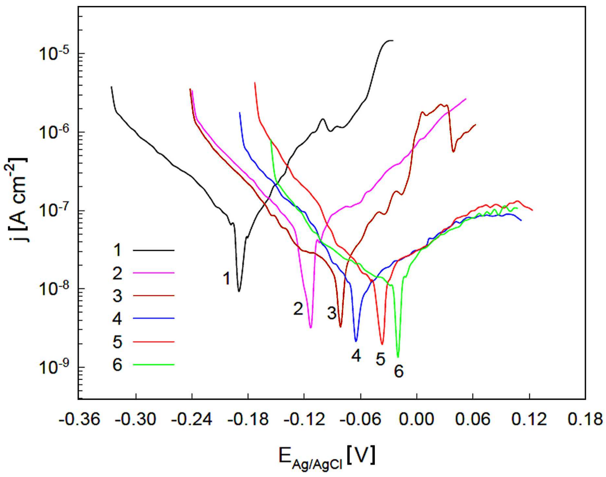

Figure 9. Polarization curves before the photochemical ageing of specimens: uncoated steel (1), with Paraloid B67 (2), with Antik Patina (3), with SiO_2:HMDS (4), with SiO_2 (5) and with Cosmolloid H80 (6)

Table 2. Electrochemical data (corrosion rate resistance, R_p, corrosion potential, E_{corr}, and corrosion current, j_{corr}) for uncoated and differently coated steel substrates before and after the photochemical ageing

No.	Coatings	Corrosion parameters					
		Before photochemical ageing			After photochemical ageing		
		R_p [Ω·cm^2]	E_{corr} [V]	j_{corr} [µA/cm^2]	R_p [Ω·cm^2]	E_{corr} [V]	j_{corr} [µA/cm^2]
1	Uncoated steel specimen	87	-0.195	8.5	148	-0.175	9.5
2	Paraloid B67	156	-0.116	5.8	154	-0.158	7.6
3	Antik Patina	310	-0.095	2.1	300	-0.140	6.2
4	Alkaline 3 mas.% SiO2 with HMDS	374	-0.057	1.1	1462	-0.024	2.2
5	3 mas.% SiO2	430	-0.038	0.8	581	-0.057	3.2
6	Cosmolloid H80	474	-0.024	0.8	327	-0.059	5.0

coated sample. Referring to the data in Table 2, it can be stated that between coatings the worst protective coating is obtained from Paraloid B67. Additionally, corrosion parameters indicate that the Cosmolloid H80 and colloidal silica coatings are likely to be the most effective steel protections against environmental impact. Electrochemical data after the photochemical ageing revealed that the uncoated steel specimen is poorly and least protected (R_p = 148 Ω·cm^2; E_{corr} = −0.175 V; j_{corr} = 9.5 µA/cm^2). Among these coatings, Paraloid B67 and Antik Patina do not protect the steel surface enough as corrosion parameters changed rapidly after the photochemical ageing. The data of the Cosmolloid H80 coating intensely decreased after the photochemical ageing as well. The alkaline 3 mas.% SiO_2 coating after the ageing retained or only slightly changed the corrosion parameters. Assuming all electrochemical data, it can be concluded that the nano-silica modified with HMDS coating can be successfully applied for the protection of steel surface as all the corrosion parameters after the photochemical ageing remained in good quality.

IV. Conclusions

The novel sol-gel route for the conservation of steel surface was suggested. The methyl-modified silica coatings were obtained using tetraethylorthosilicate (TEOS) as a precursor and hexamethyldisilozane (HMDS) as modifying agent. It was demonstrated that coating obtained from alkaline 3 mas.% SiO_2 and modified with HMDS are highly hydrophobic with contact angle of 150.7°. For the comparison, the steel substrates were also coated with commercial polymers Paraloid B67, Cosmolloid H80 and Antik Patina which are used in the conservation of cultural heritage. Among the polymeric coatings Cosmolloid H80 showed the highest contact angle value (128.5°). Morphological SEM investigations revealed that after the photochemical ageing intensive dark spots appeared in the coatings that are obtained from Cosmolloid H80 and Antik Patina. Moreover, the coatings obtained from Paraloid B67 were strongly cracked before and after ageing. The microstructure of the nano-silica coatings modified with HMDS was different with smooth and even surface. Moreover, the specific network of light spots, having size of 1–5 µm was formed on the surface of the coatings after the photochemical ageing. Evaluation of the photochemical impact indicated the degradation of hydrophobicity and corrosion parameters in all coatings. However, the best electrochemical data is retained in the SiO_2 coating modified with HMDS. It can be concluded that protective HMDS modified silica coatings on steel substrate could be applied for the conservation of steel at ambient conditions.

Acknowledgements: The study was funded from the European Community's social foundation under Grant Agreement No. VP1-3.1-ŠMM-08-K-01-004/KS-120000-1756.

References

1. L. Bamoulid, M.-T. Maurette, D. De Caro, A. Guenbour, A. Ben Bachir, L. Aries, S. El Hajjaji, F. Benoît-Marquié, F. Ansart, "An efficient protection of stainless steel against corrosion: Combination of a conversion layer and titanium dioxide deposit", *Surf. Coat. Technol.*, **202** (2008) 5020–5026.
2. N.K. Huang, H. Kheyrandish, J.S. Collignon, "Microstructure of zirconia films prepared by argon ion beam enhanced deposition", *Phys. Status Solidi*, **132** (1992) 405–411.
3. L. Gal-Or, I. Silberman, R. Chaim, "Electrolytic ZrO_2 coatings: I. Electrochemical aspects", *J. Electrochem. Soc.*, **138** (1991) 1939–1942.
4. S.K. Tiwari, R.K. Sahu, A.K. Pramanick, R. Singh, "Development of conversion coating on mild steel prior to sol gel nanostructured Al_2O_3 coating for enhancement of corrosion resistance", *Surf. Coat. Technol.*, **205** (2011) 4960–4967.
5. V.V. Vargin, *Technology of Enamels*, Ed. by K. Shaw, MaClaren & Sons, London, 1967, pp. 27–84
6. S.J. Bull, R. Kingswell, K.T. Scorr, "The sliding wear of plasma sprayed alumina", *Surf. Coat. Technol.*, **82** (1996) 218–225.
7. E. W. Brooman, "Modifying organic coatings to provide corrosion resistance – Part III: Organic additives and conducting polymers", *Metal Finish.*, **100** [6] (2002) 104–110.
8. E.W. Brooman, "Modifying organic coatings to provide corrosion resistance: Part II – Inorganic additives and inhibitors", *Metal Finish.*, **100** (2002) [5] 42–53.
9. H. Wang, R. Akid, "Encapsulated cerium nitrate inhibitors to provide high-performance anti-corrosion sol-gel coatings on mild steel", *Corros. Sci.*, **50** (2008) 1142–1148.
10. Y. Xie, H.M. Hawthorne, "Wear mechanism of plasma-sprayed alumina coating in sliding contacts with harder asperities", *Wear*, **90** (1999) 225–229.
11. R. Yılmaz, A.O. Kurt, A. Demir, Z. Tatlı, "Effects of TiO_2 on the mechanical properties of the Al_2O_3-TiO_2 plasma sprayed coating", *J. Eur. Ceram. Soc.*, **27** (2007) 1319–1323.
12. H. Lin, Y. Zeng, C.X. Ding, P.Y. Zhang, "Effects of temperature on tribological properties of nanostructured and conventional Al_2O_3-3wt.% TiO_2 coatings", *Wear*, **256** (2004) 1018–1025.
13. K.J. Chabrol, J.P. Bonino, M. Gressier, M.J. Menu, N. Pébčre, "Improvement of barrier properties of a hybrid sol-gel coating by incorporation of synthetic talc-like phyllosilicates for corrosion protection of a carbon steel", *Surf. Coat. Technol.*, **206** (2012) 2884–2891.
14. P. Galliano, J.J. Damborena, M.J. Pascual, A. Duran,

"Sol-gel coatings on 316L steel for clinical applications", *J. Sol-Gel Sci. Technol.*, **13** (1998) 723–727.
15. D.C.L. Vasconcelos, J.A.N. Carballo, M. Mantel, W.L. Vasconcelos, "Corrosion resistance of stainless steel coated with sol-gel silica", *J. Non-Cryst. Solids*, **273** (2000) 135–139.
16. S. Ono, H. Tsuge, Y. Nishi, S.I. Hirano, "Improvement of corrosion resistance of metals by an environmentally friendly silica coating method", *J. Sol-Gel Sci. Technol.*, **29** (2004) 147–153.
17. W.J. van Ooij, D. Zhu, M. Stacy, A. Seth, T. Mugada, J. Gandhi, P. Puomi, "Corrosion protection properties of organofunctional silanes – An overview", *Tsinghua Sci. Technol.*, **10** (2005) 639–664.
18. D. Wang, G.P. Bierwagen, "Sol-gel coatings on metals for corrosion protection", *Prog. Org. Coat.*, **64** (2009) 327–338.
19. E. Kiele, J. Lukseniene, A. Griguceviciene, A. Selskis, J. Senvaitiene, R. Ramanauskas, R. Raudonis, A. Kareiva, "Methyl-modified hybrid organic-inorganic coatings for the conservation of copper", *J. Cult. Herit.*, **15** (2014) 242–249.
20. M.A. Sainz, A. Durán, J.M. Fernández Navarro, "UV highly absorbent coatings with CeO_2 and TiO_2", *J. Non-Cryst. Solids*, **121** (1990) 315–318.
21. M. Guglielmi, "Sol-gel coatings on metals", *J. Sol-Gel Sci. Technol.*, **8** (1997) 443–449.
22. P. Innocenzi, M. Guglielmi, M. Gobbin, P. Colombo, "Coating of metals by the sol-gel dip-coating method", *J. Eur. Ceram. Soc.*, **10** (1992) 431–436.
23. W. Boysen, A. Frattini, N. Pellegri, O. de Sanctis, "Protective coatings on copper prepared by sol-gel for industrial applications", *Surf. Coat. Technol.*, **122** (1999) 14–17.
24. J. Pilipavicius, I. Kazadojev, A. Beganskiene, A. Melninkaitis, V. Sirutkaitis, A. Kareiva, "Hydrophobic antireflective silica coatings via sol-gel process", *J. Mater. Sci.*, **14** (2008) 283–287.
25. O. Chiantore, M Lazzari, "Photo-oxidative stability of paraloid acrylic protective polymers", *J. Polym.*, **42** (2001) 17–27.
26. D. Chelazzi, A. Chevalier, G. Pizzorusso, R. Giorgi, M. Menu, P. Baglioni, "Characterization and degradation of poly(vinyl acetate)-based adhesives for canvas paintings", *Polym. Degrad. Stab.*, **107** (2014) 314–320.
27. M. Lazzari, O. Chiantore, "Thermal-ageing of paraloid acrylic protective polymers", *J. Polym.*, **41** (2000) 6447–6455.
28. P. Kotlík, K. Doubravová, J. Horálek, L. Kubáč, J. Akrman, "Acrylic copolymer coatings for protection against UV rays", *J. Cult. Herit.*, **15** (2014) 44–48.
29. C. Milanesi, F. Baldi, S. Borin, L. Brusetti, F. Ciampolini, F. Iacopini, M. Cresti, "Deterioration of medieval painting in the chapel of the Holy Nail, Siena (Italy) partially treated with Paraloid B72", *Int. Biodeter. Biodegr.*, **63** (2009) 844–850.
30. G.M. Crisci, M.F. La Russa, M. Malagodi, S.A. Ruffolo, "Consolidating properties of Regalrez 1126 and Paraloid B72 applied to wood", *J. Cult. Herit.*, **11** (2010) 304–308.