VILNIUS UNIVERSITY
CENTER FOR PHYSICAL SCIENCES AND TECHNOLOGY
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DEVELOPMENT AND APPLICATION OF NEW METHODS FOR THE CONSERVATION OF METAL CULTURAL HERITAGE ARTICLES

Summary of Doctoral Dissertation

Physical sciences, Chemistry (03 P)

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CHEMIJOS INSTITUTAS

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1. INTRODUCTION

Metals conservation involves the preservation of cultural objects. The goal is to preserve objects while retaining evidence of their cultural context and integrity. Ideally there should be a minimum change to an object while achieving this and restoration to the former state is rarely carried out. While preservation appears to be a straight forward materials science problem, involving elucidation of the structure and corrosion of metals to develop conservation procedures that prevent or control corrosion, it is constrained by ethics, aesthetics, and cultural contexts that may complicate, constrain, and ultimately direct preservation strategies. The goal of conservation is the preservation of an object using minimum intervention. Research into the corrosion and conservation of historic and archaeological metals is developing significantly due to the increasing contribution of dedicated specialists that have a specific focus and the challenges of large complex objects.

Copper, bronze, brass and steel were commonly employed in cultural heritage objects. They were commonly used in cultural heritage objects such as sculptures, other outdoor decorative items, swords, details of appearing, jewelry, etc. Corrosion inhibitors, polymer and synthetic wax coatings are used for the conservation of metal objects. However, these methods do not provide successful preservation of metals for a longer term. Researchers are mainly focused on obtaining long–term, anticorrosion, protective coatings and methods that could replace toxic solutions used in conservation and restoration of metals.

Sol–gel derived coatings have already been applied for surface protection of metal specimens. However, the properties of the coatings may diverge on different metal substrates. Namely, sol-gel method is highly perspective for obtaining thin, hydrophobic, anticorrosion coatings with great chemical stability, oxidation control and enhanced corrosion resistance on metal substrates. Moreover, sol–gel method is not toxic, has low costs in the process and equipment, has no limits in the size or shape of the substrates and etc.

In order to compare the efficiency of proposed sol-gel method metal substrates were also coated with substances that are used in conservation of metals: Paraloid B72, Plexisol P550-40, polyvinyl butyral (PVB), Paraloid B67, Cosmolloid H80 and Antik Patina. The hydrophobicity of obtained coatings was evaluated by contact angle measurements. The morphological features of just obtained and photochemically aged coatings on the metal substrates were determined by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The corrosion parameters were obtained by potentiodynamic polarization measurements.

The main aim of this doctoral thesis: to apply a novel sol-gel route for the preservation of metals and metal alloys.

Formulated tasks of thesis are as follows:

1. To ascertain the optimal parameters of a novel sol-gel route on a surface of glass.
2. To obtain sol-gel derived coatings on the surface of copper and investigate the suitability of sol-gel method for the conservation of copper.
3. To obtain sol-gel derived coatings on the surface of steel and investigate the suitability of sol-gel method for the conservation of steel.
4. To obtain sol-gel derived coatings on the surface of bronze and brass, and investigate the suitability of sol-gel method for the conservation of bronze, brass.

2. EXPERIMENTAL

2.1. Preparation of sols

The colloidal silica sols were prepared using tetraethylorthosilicate (TEOS; Fluka, ≥98 %) as a starting material. 3% SiO_2 was obtained by alkaline and acidic catalysis using ethanol (EtOH) as a solvent and NH_3 or HCl as a catalyst. The molar ratio of components during acidic catalysis was selected to be TEOS:HCl:H_2O:EtOH = 1:0.0001:2.37:38. In order to complete hydrolysis, obtained sol was aged for 7 days at 25 °C. The molar ratio of components during alkaline catalysis was TEOS:NH_3:H_2O:EtOH = 1:0.2:2.37:37.48. In this case, sol was aged for 19 days at the same temperature.

These SiO_2 sols were used in further coating and modification (in order to prepare methyl–modified coatings) processes. Acidic silica sol was used for the modification with trimethylchlorosilane (TMCS; Sigma Aldrich, ≥98 %) and alkaline sol was used for the modification with hexamethyldisilozane (HMDS; Sigma Aldrich, ≥98 %). Two ways of preparation of methyl–modified copper surfaces were suggested.

Two routes were applied for copper substrates: 1. the modification of colloidal nanosilica was performed in liquid phase following the dip-coating of copper substrates; 2. the obtained silica coatings on copper substrates were treated with TMCS and HMDS solutions – modification on the surface of SiO_2 coating. Methyl-modified coatings were obtained after the modification of SiO_2 sols. Acidic catalysis (Figs. 1a and 2a) was used to obtain the coatings on copper substrates. Alkaline catalysis (Figs. 1b and 2b) was used to attain the coatings on copper, steel, bronze and brass substrates.

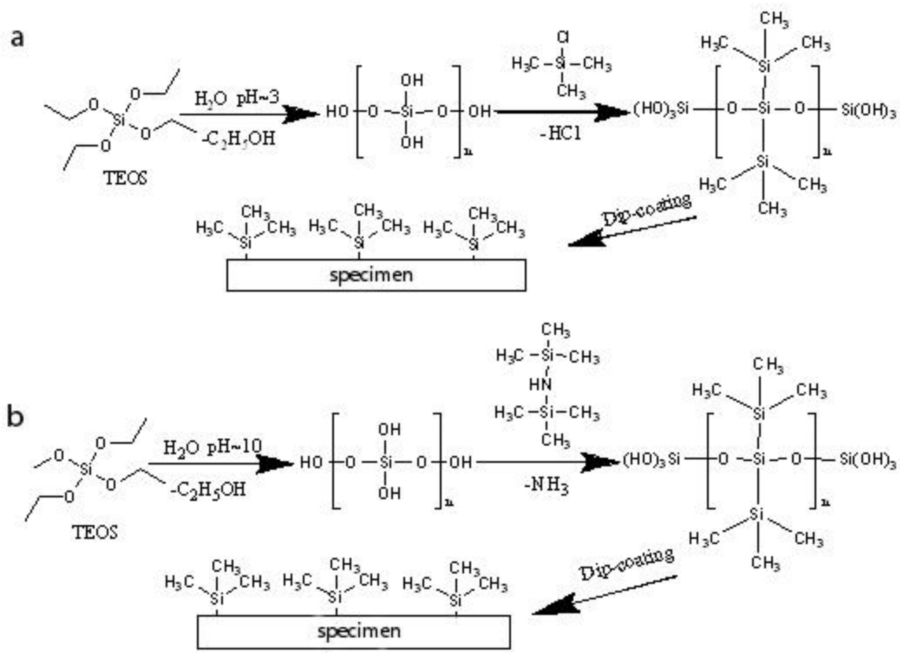

Fig. 1. Synthesis scheme of 3 % SiO_2: a. acidic catalysis, modification with TMCS; b. alkaline catalysis, modification with HMDS. Modification in a liquid phase

2.2. Preparation of solutions

In order to compare the quality of coatings derived from polysiloxane, the polymeric coatings that are widely used in conservation of metals (Paraloid B72, Plexisol P550-40, polyvinyl butyral (PVB), Paraloid B67, Cosmolloid H80 and Antik Patina obtained from Kremer Pigmente GmbH & Co) were applied on copper substrate. The following concentrations of polymers were used in the formation of polymeric coatings: 1 mass % Paraloid B 72 in ethanol, 2 mass % Plexisol P550-40 in acetone, 0.5 mass% PVB in ethanol, 1 mass % Paraloid B67 in acetone, 6 mass % Cosmolloid H80 in toluene and 10 mass % Antik Patina in white spirit. Solutions were aged at a room temperature (25^{o}C) for 2 days.

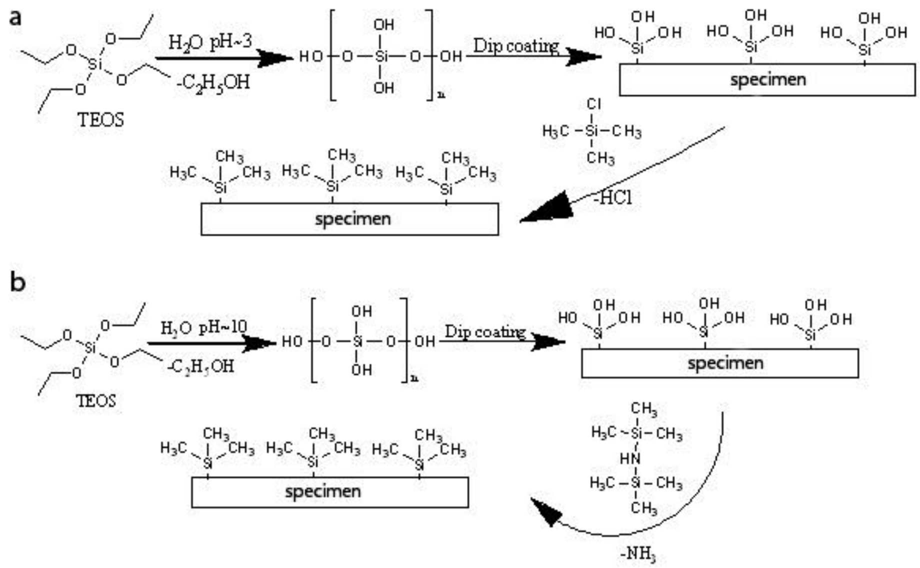

Fig. 2. Synthesis scheme of 3 % SiO_2: a. acidic catalysis, modification with TMCS; b. alkaline catalysis, modification with HMDS. Modification on the coating's surface

2.3. Preparation of films

Different protective coatings were deposited on copper (1.7 x 5.0 cm), which had been cleaned with 1 % sulphuric acid, mechanically treated with steel wool and then washed with ethanol. Steel (1 x 1.5 cm, 0.5 mm thick steel foil, Alfa Aesar), bronze (Cu 89.0-91.0%; Sn – remainder) and brass (Cu 68.5-71.5%; Zn – remainder) substrates (1 x 1.5 cm, 1 mm thick bronze and brass foil, Alfa Aesar) were treated mechanically with aluminium oxide paper and then washed with ethanol. The dip-coating technique was used to prepare the sol-gel derived and polymer coatings on metal substrates. Coatings were deposited on metal specimens by the dip-coating process: pre-treated metal substrate was immersed into the sol or solution by the speed of 85 mm/min. Metal sample retained in the solution for 20 s and followed by withdrawal of the pre-treated metal 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.

2.4. Artificial ageing

Sol-gel derived and polymer (used in conservation) coatings were exposed to artificial ageing in a photochemical reactor. Philips luminescence lamps PL–9W110 of 40 W that emit in the range of 320–400 nm were used in a photochemical reactor. The specimens were placed 0.5 m above the lamps. The temperature in the reactor was 36–40 °C, relative humidity –36–40%.

The samples had been aged for 28 days.

2.5. Characterization and measurements

Coatings were characterized by contact angle measurements as static contact angles were evaluated at ten different positions for each sample, and the average value was accepted as the contact angle (Contact Angle Meter KSV Instruments CAM – 100). Characterization of coatings was also performed using FTIR (PerkinElmer Frontier FT-IR with ATR module) spectroscopy. Scanning electron microscopy (SEM; Hitachi TM3000) and atomic force microscopy (AFM; Bioscope II, Veeco) were also performed on the bare and coated substrates to characterize the surface morphology. The size of the particle were evaluated by Dynamic light scattering (DLS, Malvern Zetasizer Nano ZS) method. Electrochemical tests were also done to evaluate corrosion parameters: j_{corr} – corrosion current, E_{corr} – corrosion potential, R_p – corrosion rate resistance. 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°Ag/AgCl = 0.197 V. Using referred methods, bare and coated substrates before and after the photochemical ageing were compared.

3. RESULTS AND DISCUSSIONS

3.1 Deposition of the coatings on glass specimens

In order to ascertain optimal parameters of sol-gel processing, concentrations of TMCS and HMDS coatings were formed on glass specimens. Two sols were formed with molar ratio: a. acidic catalysis TEOS:HCl:H_2O:EtOH=1:0,0001:2,37:38; b. alkaline catalysis TEOS:NH_3:H_2O:EtOH=1:0,2:2,37:37,48. Surface and liquid modification of hydrolyzed intermediate was performed (synthesis mechanisms are presented in Figs. 1 and 2) with HMDS and TMCS. Same sols and coatings were applied on copper substrates thus in this summary deposition on copper substrate is presented.

3.2. Deposition of the coatings on copper specimens

Tetraethylorthosilicate (TEOS; Fluka, ≥98 %) was used in the preparation of colloidal silica sols, while ethanol (EtOH) and HCl or NH_3 were used as solvent and catalysts, respectively.

3% SiO_2 sol was obtained by acidic and alkaline catalysis. Preparation of sols is described in Experimental part.

In order to compare the quality of coatings derived from polysiloxane, the polymeric coatings that are widely used in conservation of metals – Paraloid B 72, Plexisol P 550-40 and polyvinyl butyral (PVB) were obtained from Kremer Pigmente GmbH & Co and also applied on copper substrate. The following concentrations of polymers were used in the formation of polymeric coatings: 1 mass % Paraloid B 72 in ethanol, 2 mass % Plexisol P550-40 in acetone and 0.5 mass% PVB in ethanol. Solutions were aged at a room temperature for 2 days. Measurements were performed prior to and after the photochemical ageing.

3.2.1. FTIR spectroscopy

The structure of coatings was evaluated by FTIR spectroscopy. In Fig. 3 (I) FTIR spectra of pure SiO_2 and SiO_2 modified with HMDS before the photochemical ageing is presented. 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 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. Absorption bands of Si–O, C–H ir O–H in pure SiO_2 coating remain after the photochemical ageing (see Fig. 3, II). However, additional bands in the range of 1500 cm^{-1} to 1700 cm^{-1} appear. The exact origin of these bands is not known. However, the presence of these bands indicates of the destruction process in the coating. On another hand, spectra of SiO_2 modified with HMDS remains unchanged after the photochemical ageing. Vibrations and intensities of Si–O (1089 cm^{-1} and 804 cm^{-1}), Si–OH (976 cm^{-1}) and C–H (2955 cm^{-1}, 1445 cm^{-1}) are observed. Thus, FTIR results indicate that SiO_2 coating modified with HMDS, is highly resistance to photochemical ageing.

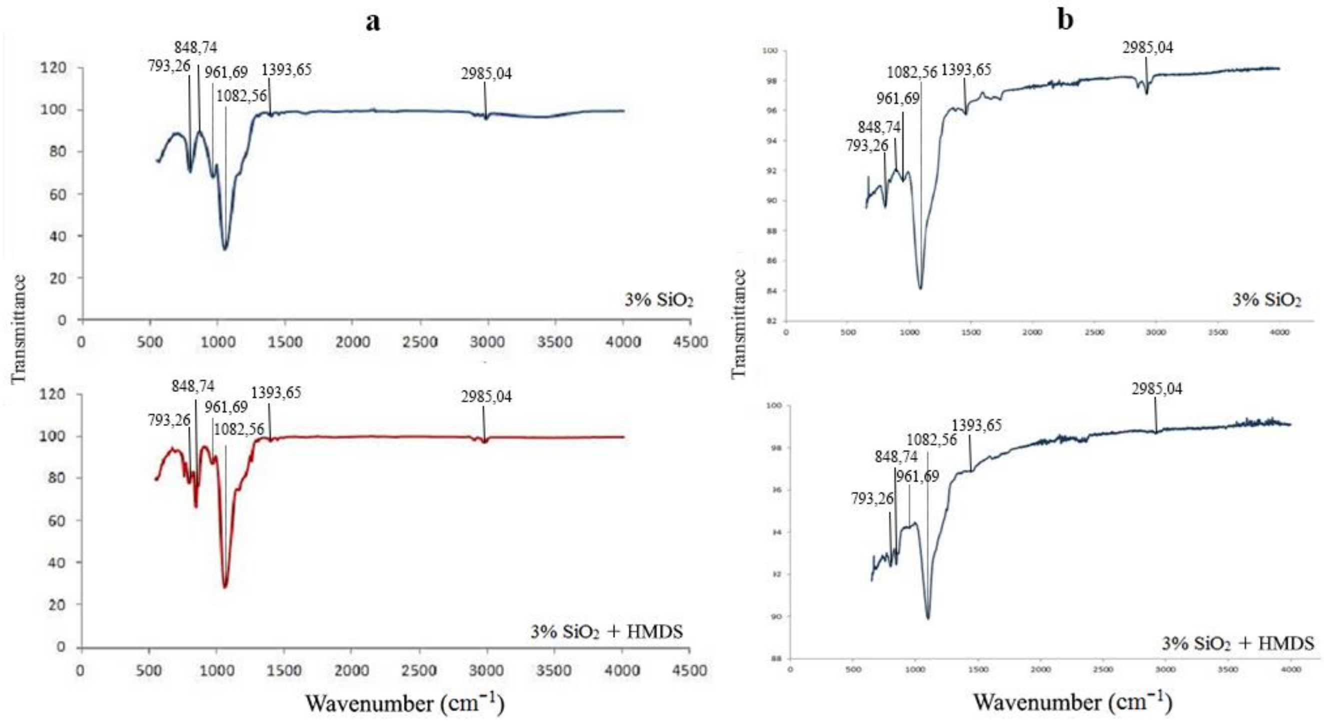

Fig. 3. FTIR spectra of SiO_2 and SiO_2 modified with HMDS a. before and b. after the photochemical ageing

3.2.2. Contact angle measurements

All copper specimens were artificially aged. The colour of copper is not affected strongly by the coatings. It means, that reddening of copper does not proceed and corrosion compounds do not form during sol-gel conservation and deconservation processes. As was mentioned in the Experimental part, the coated samples were aged at certain conditions in a photochemical reactor for 14 days. In this part, periodical photo fixation and contact angle measurements were performed. According to visual observation, the photochemical aging had a negative impact on the surface of conserved copper. However, the seriousness of influence could be determined only after physico-chemical characterization of surfaces. Namely, the results from contact angle measurements revealed that all coatings more or less were affected by photochemical ageing. The results demonstrating the degree of hydrophobicity of obtained surfaces are shown in Table 1.

As seen from Table 1, the hydrophobicity of uncoated copper surface remained almost the same after aging the specimen for 14 days. Surprisingly, acidic conditions of preparation nanosilica coatings on copper substrates ensured formation of more hydrophilic surfaces before and after modification even before aging. For example, when silica surfaces obtained from acidic medium were modified on the surface with 10% TMCS, the determined contact angle was only 63.0 ^{o}. Moreover, the contact angle of non-modified silica surface was 69.5 ^{o}. On the other hand, acidic 3% SiO_2 modification in liquid phase with 6% TMCS produced coatings with contact angle of 113.5 ^{o}, which was higher than that of 78.8 ^{o} of the uncoated copper substrate.

Table 1. The contact angles determined on different copper surfaces before and after photochemical aging.

No.	Coating conditions	Before aging	After aging for 14 days
1.	Cleaned uncoated copper surface	83.0(5)	83.6(9)
2.	Acidic; route 2; with 10% TMCS	63.0(6)	62.0(7)
3.	Acidic; no modification	69.5(8)	64.0(7)
4.	1% Paraloid B 72	72.1(6)	65.3(6)
5.	0.5% PVB	82.3(4)	75.9(5)
6.	Acidic; route 2; with 10% HMDS	94.8(8)	78.1(7)
7.	2% Plexisol P 550-40	95.6(9)	68.8(8)
8.	Acidic; route 1; with 6% TMCS	113.5(6)	84.3(7)
9.	Alkaline; no modification	128.4(7)	89.3(7)
10.	Alkaline; route 2; with 10% HMDS	128.9(5)	82.6(7)
11.	Alkaline; route 1; with 8% HMDS	132.7(4)	87.9(5)
12.	Alkaline; route 2; with 10% TMCS	135.9(8)	122.2(6)

Apparently, the coatings obtained from 1% Paraloid B 72 and 0.5% PVB ethanolic solutions were hydrophilic. The hydrophobicity of copper surface increased up to 95.6 ^{o} by coating with Plexisol P 550-40. The highest contact angle value before the photochemical ageing was observed in copper specimen coated with modified SiO_2 coatings in alkaline media. The nanosilica particles with higher specific surface area and hydroxyl content have formed during alkaline catalysis. Consequently, they could be grafted with more TMCS and HMDS than those obtained at acidic conditions. When silica surfaces were modified in a liquid phase with 8 % HMDS, the determined contact angle was 132.7 ^{o}. The modification of nanosilica coating obtained also from alkaline media with 10% TMCS immediately on the surface gave contact angle value of 135.9 ^{o}. Evidently, all coatings were significantly affected by photochemical ageing. However, the contact angle of TMCS modified coating obtained from alkaline media remained rather high (122.2 ^{o}) even after ageing. This could be clearly illustrated by the change of water droplet placed on the coating.

Thus, the results obtained by contact angle measurements let us to conclude that methyl–modified silica coatings for the protection of the external surface of copper show different hydrophobicity of the films depending on the selected sol-gel processing route. For further morphological characterization only copper specimens which showed higher contact angles values were selected.

3.2.3. Scanning electron microscopy

The morphological analysis of the obtained film surfaces was performed by SEM analysis. Fig. 4 presents the SEM images of the SiO_2 coating prepared using alkaline conditions and modified with 10% TMCS (alkaline catalysis). The surface of TMCS modified films consists of particles of different shape less than 1 μm in size.

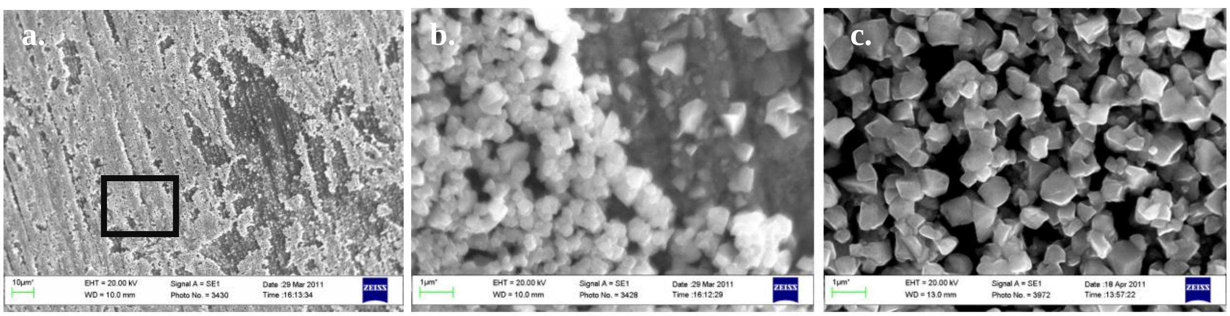

Fig. 4. SEM micrographs of alkaline SiO_2 modified with 10% TMCS a., b. before and after c. photochemical aging

As seen from Fig. 4, the surface morphology of film is slightly affected by photochemical aging. Interestingly, the cubic grains with slightly increased size have formed on the surface after aging. The EDX analysis of different areas of samples revealed that the coatings which were modified with TMCS contained chlorine prior and after the photochemical ageing. The SEM micrograph of coating (alkaline with 10% TMCS) before photochemical ageing and obtained at lower magnification is presented in Fig. 4a. The area where the concentration of chlorine was the highest is marked. This explains the high contact angle value obtained for alkaline 3% SiO_2 and TMCS modified coating after the photochemical ageing.

The SEM micrographs of the SiO_2 coatings prepared using alkaline conditions and modified with 8 % HMDS are shown in Fig. 5.

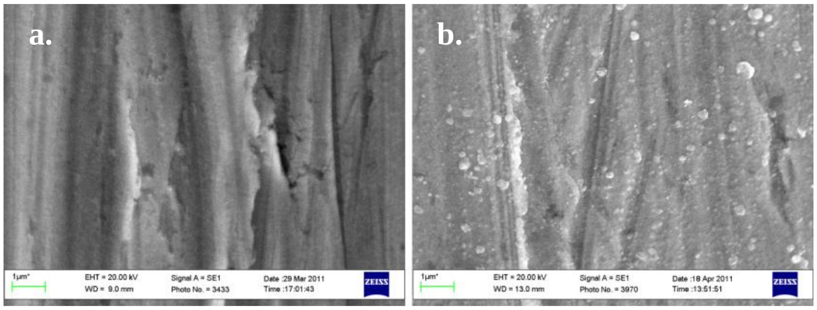

Fig. 5. SEM micrographs of coatings (alkaline with 8% HMDS) a. before and b. after photochemical aging

Fig. 5 clearly demonstrates, that the surface microstructure of HMDS modified film differs significantly from that of presented in Fig. 4. The films show a smooth and uniform surface with regular morphology. The formation of nonporous surface microstructure by modification of silica coating with HMDS might be beneficial to the preservative application. Moreover, the surface morphologies of coatings before and after aging are almost similar. However, the formation of additional nanograins on the surface after photochemical aging was also detected. The EDX analysis results showed that there is no chlorine apart expected elements.

3.2.4. Atomic force microscopy

Three-dimensional topographic AFM images of copper specimens obtained at different coating conditions are shown in Fig. 6. Clearly, the surface of bare copper plates is not very smooth and had been scratched during the cleaning process (see Fig. 6 a.). Evidently, negligible changes in surface morphology were observed after artificial aging. The AFM images of SiO_2 coating prepared using alkaline conditions and modified with 10% TMCS on the surface of the coating are shown in Fig. 6 c., d.

The roughness of the surface obtained by modification with TMCS increased significantly. Besides, the islands appeared on the surface of coating, which remain unchanged after aging. The AFM images of SiO_2 coating prepared using alkaline conditions and modified with 8 % HMDS in liquid phase are shown in Fig. 6 e., f. The SiO_2 coatings modified in the liquid phase with 8 % HMDS are sufficiently even and smooth. Moreover, the aging did not influence the roughness of the film surfaces. Therefore, from the AFM measurements, we can conclude that the surface roughness of the methyl-modified silica coatings is not responsible for the degradation of hydrophobic characteristics of films during aging.

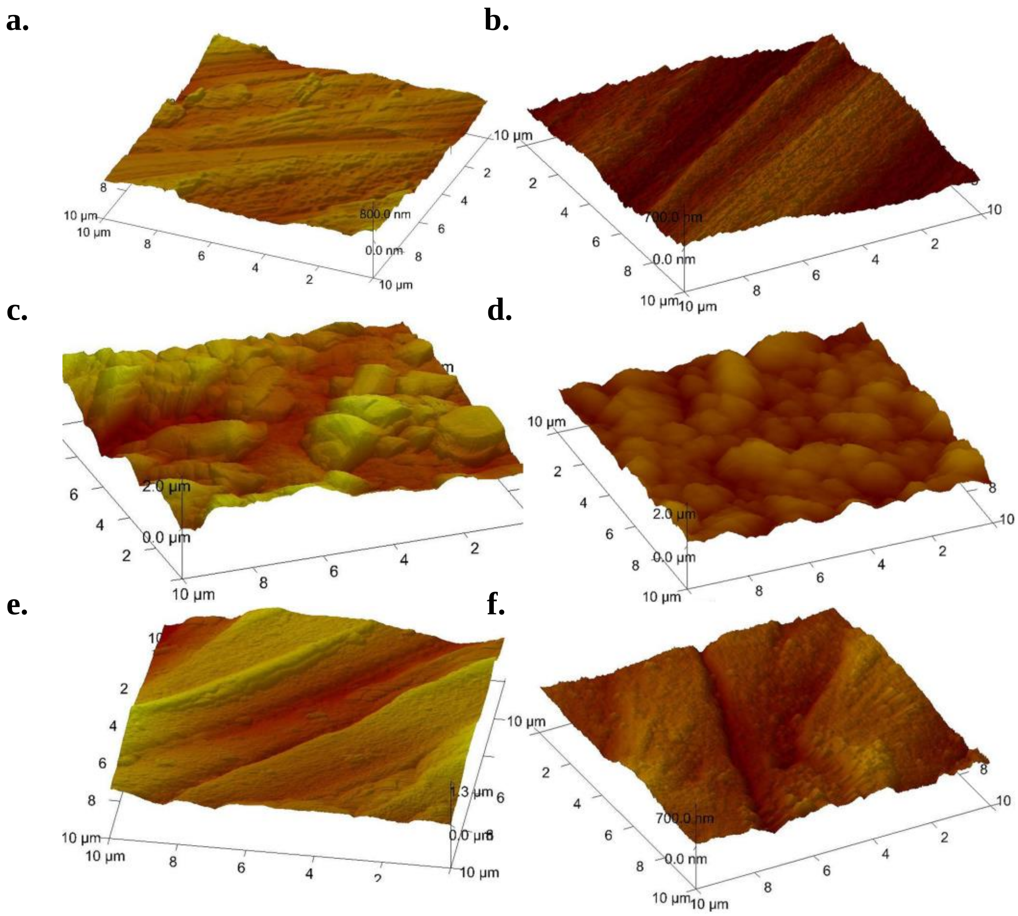

Fig. 6. AFM micrographs of cleaned copper surface a. before and b. after photochemical aging; alkaline SiO_2 modified with 10% TMCS c. before and d. after photochemical aging; alkaline SiO_2 modified in a liquid phase with 8% HMDS a. before and b. after photochemical ageing

3.2.5. Potentiodynamic polarization measurements

Potentiodynamic polarization measurements were performed in order to evaluate the corrosion parameters of the coatings on the copper substrates. Polarization curves recorded on the acidic and alkaline modified SiO_2 films (before and after photochemical ageing) are shown in Fig. 7 a. and b., respectively.

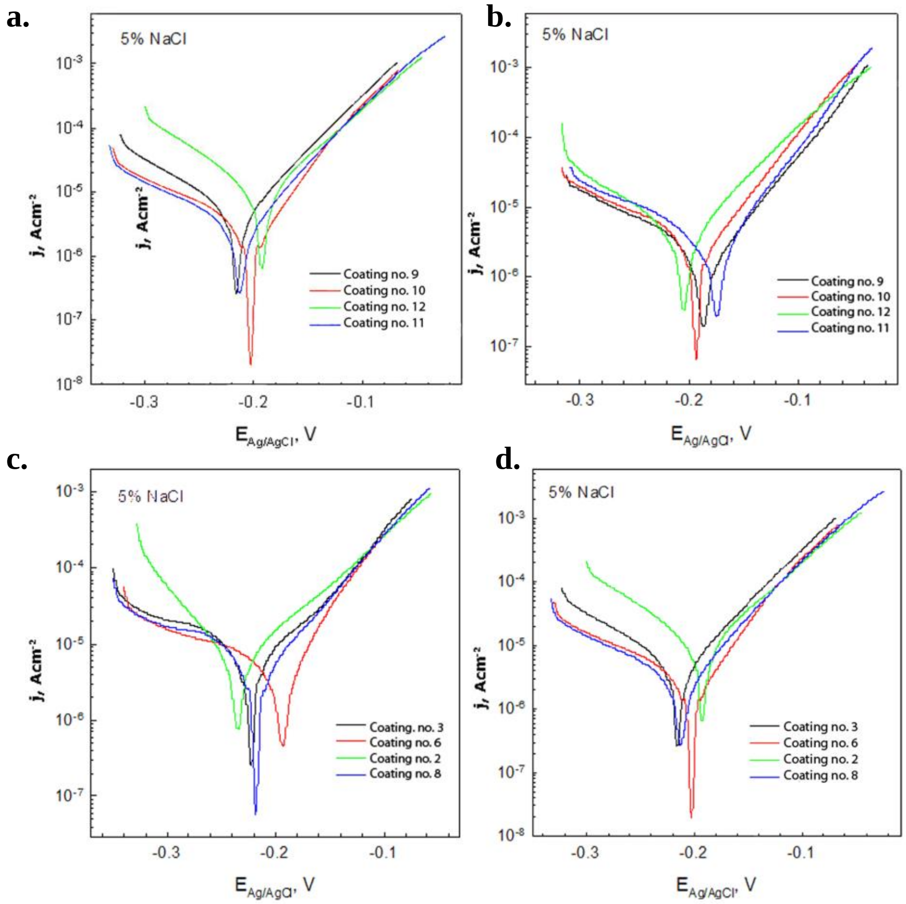

Fig. 7. Polarization curves of acidic modified SiO_2 films on copper substrates a. before and b. after photochemical aging; alkaline modified SiO_2 films on copper substrates c. before and d. after photochemical aging

It was determined that coatings modified with HMDS showed better corrosion parameters (R_p = 2796.8 Ωcm^2; E_{corr} = - 0.190 V; j_{corr} = 3.6 μAcm^{-2}). Such observation let us conclude that HMDS modified surface is more passive than the coatings modified with TMCS (R_p = 1996.8 Ωcm^2; E_{corr} = -0.204 V; j_{corr} = 8.9 μAcm^{-2}). Not modified alkaline and acidic silica coatings showed significantly less protection from the environment impact. Electrochemical measurements indicated that the coatings traditionally used in the conservation of metals are less active than the coatings formed by suggested sol-gel processing. Polarization curves also showed that the most active copper surfaces are those modified on the surface of the coating with 10 % TMCS. Referring to all electrochemical results, the modification with HMDS could be successfully used for efficient protection of the surface of copper.

3.3. *Deposition of the coatings on steel specimen*

Referring to the results obtained on copper surface only alkaline catalysis was used to deposit sol – gel derived coatings on steel substrate. Conditions, molar ratio and catalysis of sol are described in Experimental part. 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 proposed silica coatings. All the measurements were performed before and after the photochemical ageing.

3.3.1. 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 2.

Table 2. The contact angles determined on different steel surfaces before and after photochemical aging.

No	Coating conditions	Before aging	After aging for 14 days	After aging for 28 days
1	3 % SiO_2	65.2(3)	43.3(4)	35.2(1)
2	10 % *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 % *Paraloid B67*	90.8(1)	83.9(2)	83.9(2)
5	6 % *Cosmolloid H80*	128.5(3)	104.7(6)	103.8(9)
6	Alkaline 3 % SiO_2 with 8 % HMDS	150.7(7)	142.9(8)	151.2(5)

As seen from Table 2, the contact angle value of uncoated steel substrate is 88.9° and decreased until 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 nanosilica. 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 not modified nanosilica coating obtained from alkaline SiO_2 sol. This might be associated with existence of hydrophilic –OH groups on the surface of nanosilica. Obviously, the results demonstrated that contact angle value of SiO_2 coatings on steel decreased gradually until 35.2° during the photochemical ageing. Surprisingly, the contact angle value significantly increased after modification of nanosilica 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 results of contact angle measurements revealed that all the coatings were differently affected by photochemical ageing. Namely, 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 SiO_2 coating modified with HMDS (~150°).

3.3.2. Atomic force microscopy

Three-dimensional topographic AFM images revealed that surfaces of uncoated and coated with polymers specimens are rough with well pronounced scratches. However, the determined morphology of nanosilica coatings modified with HMDS was different (Fig. 8.). Evidently, 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 nanosilica gels. The roughness of the scratched surface is reduced to the minimum by applying this coating processing.

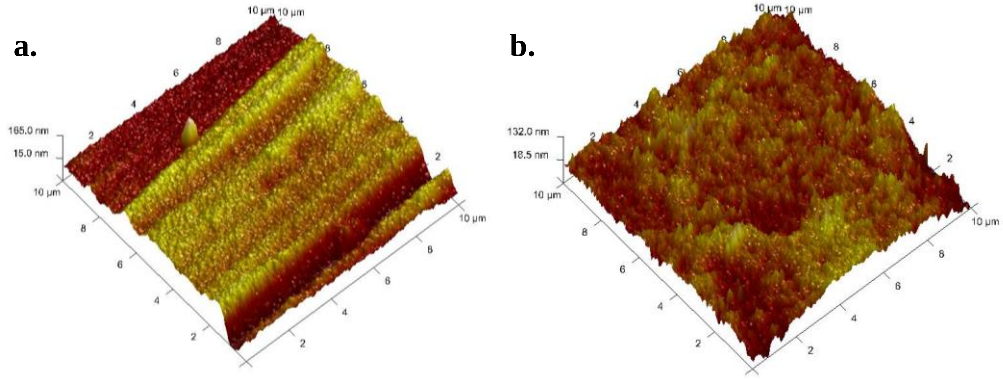

Fig. 8. AFM micrographs of steel substrate with a. SiO_2 and b. SiO_2 modified with HMDS

3.3.3. Scanning electron microscopy

SEM analysis was used to investigate morphological features of the un-coated and differently coated steel surfaces before and after the photochemical ageing. It has been noticed that sol-gel derived coatings are even, homogeneous and covers all specimen. Alkaline SiO_2 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 stays sufficiently even after the photochemical ageing.

Noticeably, coatings obtained from Cosmolloid H80 and Antik Patina before the photochemical ageing are sufficiently even 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 steel substrate in the solution of Paraloid B67 remains almost without changes after the photochemical ageing.

The SEM micrographs of the SiO_2 coatings prepared using alkaline sol-gel conditions and modified with 8 % HMDS are shown in Fig. 9.

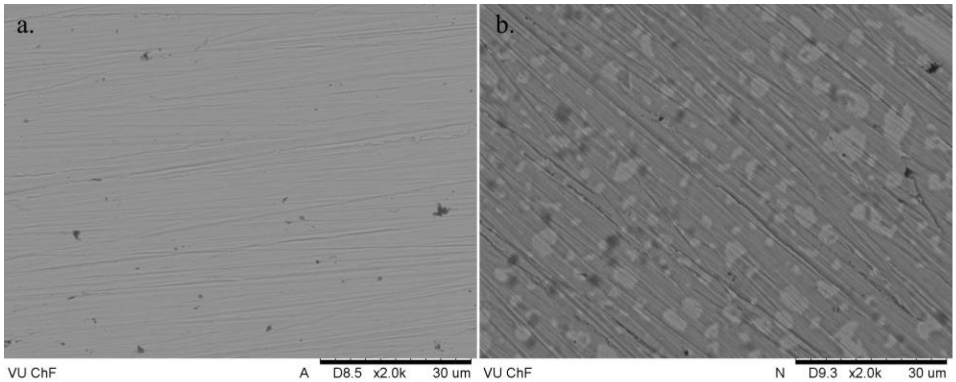

Fig. 9. SEM micrographs of steel substrates coated with HMDS modified SiO_2 a. before and b. after photochemical ageing

The microstructure of this coating slightly differs from that of without HMDS. It is noticed that surface is smooth and even with some slightly visible horizontally parallel scratches. Besides, the specific network of light spots 1–5 μm in size has formed on the surface of coating. The origin of this phenomenon is not clear but might be associated with better hydrophobic characteristics of HMDS modified nanosilica coatings.

3.3.4. Potentiodynamic polarization measurements

Corrosion parameters of the uncoated specimen and coatings on steel substrate were evaluated by performing potentiodynamic polarization measurements. The calculated data of corrosion parameters before and after the photochemical ageing is presented in Table 3.

Table 3. Electrochemical data on uncoated and differently coated steel substrates before and after the photochemical ageing.

No.	Coating conditions	Corrosion parameters					
		Before photochemical ageing			After photochemical ageing		
		R_p, Ωcm^2	E_{corr}, V	J_{corr}, μAcm^{-2}	R_p, Ωcm^2	E_{corr}, V	J_{corr}, μAcm^{-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 % SiO_2 with 8 % HMDS	374	-0.057	1.1	1462	-0.024	2.2
5.	3 % SiO_2	430	-0.038	0.8	581	-0.057	3.2
6.	Cosmolloid H80	474	-0.024	0.8	327	-0.059	5.0

As seen in Table 3, before the photochemical ageing the worst corrosion parameters are found for uncoated steel specimen. Namely, coated steel specimens are better protected from the environmental impact than uncoated sample. Referring to the data of Table 3, it can be stated that between coatings the worst protective coating is obtained from Paraloid B67. However, corrosion parameters indicate that Cosmolloid H80 and colloidal silica coatings likely are effective steel protection from environmental impact. Electrochemical data after the photochemical ageing revealed that uncoated steel specimen is poorly and least protected (R_p = 148 Ωcm^2; E_{corr} = - 0.175 V; j_{corr} = 9.5 μAcm^{-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 Cosmolloid H 80 coating intensely decreased after the photochemical ageing as well. Alkaline 3 % SiO_2 retained only slightly changed or similar corrosion parameters after the ageing. Assuming all the electrochemical data, it can be concluded that nanosilica 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.

3.3 Deposition of the coatings on bronze and brass specimen

Referring to the results obtained on copper and steel surface only alkaline catalysis was used to deposit sol – gel derived coatings on copper alloys. Conditions, molar ratio and catalysis of sol are described in Experimental part. Polymeric and bitumen coatings were not used to compare the properties with silica coatings as previous experimental data confirmed that coatings derived from sol-gel can be applied for conservation of copper and steel. All the measurements were performed before and after the photochemical ageing.

3.4.1. Contact angle measurements

Bare, coated bronze and brass specimens were aged in a photochemical reactor under the conditions described in the Experimental part. Periodic contact angle measurements and photo-fixation have been performed. Regarding to visual observations (colour, surface smoothness, cracks or scratches) bronze and brass specimens were not affected promptly. It has been only noticed that coatings became more opaque. In order to evaluate the influence of artificial ageing to the hydrophobicity of the coatings, the results of contact angle measurements have been summarized in Table 4.

Table 4. The contact angles determined on uncoated and differently coated bronze and brass specimens before and after photochemical aging

No.	Coating conditions	Contact angle [°]		
		before aging	after aging for 14 days	after aging for 28 days
	Bronze			
1.	Uncoated specimen	105.42(3)	103.13(1)	95.14(8)
2.	3 mas.% SiO_2	33.43(4)	29.05(6)	37.76(4)
3.	Alkaline 3 mas.% SiO_2 with HMDS	123.46(2)	136.42(1)	136.07(3)
	Brass			
4.	Uncoated specimen	94.29(2)	76.54(1)	45.96(7)
5.	3 mas.% SiO_2	32.36(4)	21.22(3)	24.26(9)
6.	Alkaline 3 mas.% SiO_2 with HMDS	123.20(1)	131.52 (1)	141.20(1)

Table 4 indicates that contact angle value of bare bronze specimen is comparatively high – 105.42°. However, during the artificial ageing it decreases till 95.14°. The bronze remains, however, hydrophobic enough as it is noted that hydrophobic surface is at least of 95°. Interestingly, brass is less hydrophobic as the contact angle value of bare brass is 94.29° and decrease rapidly until 45.96 after the artificial ageing. Thus, it can be stated that brass is more sensitive to the adverse influence than bronze. Apparently, the least value of contact angle both in bronze and brass specimens (33.43° and 32.36°) was determined for not modified nanosilica coating obtained from alkaline SiO_2 sol. This might be related with existence of hydrophilic –OH groups on the surface of nanosilica. The value decrease gradually during the photochemical ageing and reach 24.26° on brass substrate. However, the value slightly increases after the artificial ageing on bronze substrate (37.76°). Notably, the contact angle value significantly increased after silica sol's modification with HMDS (~123°) on both bronze and brass specimens. The HMDS modified coating on bronze and brass surface remained hydrophobic even after photochemical ageing for 28 days.

Namely, not modified nanosilica coatings are not suitable for the conservation of copper alloys as the hydrophilic surface is attained. However, the analysis revealed that HMDS modified coatings are obtained with a high contact angle value which is at least 20° or 30° higher than the polymeric coatings that are widely used in conservation of metals. To compare with, the 2 % Plexisol P 550-40 coating on copper substrate before the photochemical ageing is hydrophobic (95.6°) but decrease until 68.8° after the artificial ageing. Moreover, it was demonstrated that the coating obtained of 6 % Cosmolloid H80 is more hydrophobic (128.5°) than other coatings and remains hydrophobic after the photochemical ageing – 103.8°. But none of these coatings does keep at least 120° after the artificial ageing.

3.4.2. Atomic force and scanning electron microscopy

Atomic force microscopy observations revealed that the surfaces of bare specimens are rough (Fig. 10 a, b). AFM analysis has shown that nanosilica coatings repeated the unevenness of the surface. However, AFM also revealed that methyl-modified coatings were different, and coated specimens were more even (Fig. 10 c, d). Notably, artificial ageing slightly affected the surface of the coatings: brass and bronze surfaces became a bit rougher. This observation might indicate that after the photochemical ageing the coatings remain thinner. Moreover, rougher surface gives a higher contact angle value.

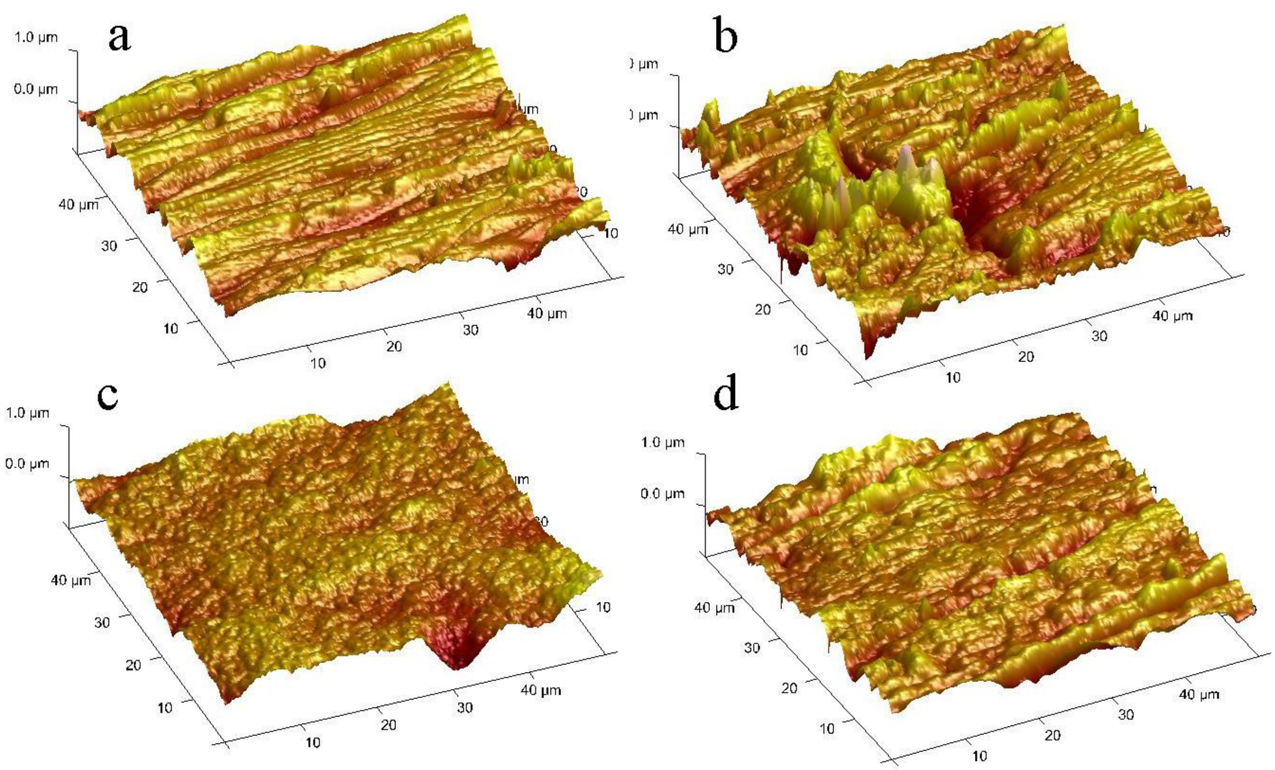

Fig. 10. AFM images of bare bronze (a) and brass (b) specimens, and bronze (c) and brass (d) coated with HMDS modified silica prior to artificial ageing

SEM analysis was performed to inquire morphological characteristics of the bare and coated metal samples prior to and after the photochemical ageing. No fractures or cracks are noticed on the surface of coated brass and bronze specimens. SEM analysis revealed that the HMDS modified SiO_2 coatings are even. However, obscure shadows on the surface of the coatings could be observed and may indicate the unevenness of the coating. Referring to SEM analysis, bare bronze and brass specimens, and HMDS modified coatings remain nearly the same after the photochemical ageing as only slight increase of roughness is noticed. Some black spots are noticed on bronze substrate prepared using alkaline conditions after the photochemical ageing. However, these dark spots are not observed on any other surface after the ageing. The origin of these dark spots might be associated with possible formation of surface corrosion products.

3.4.3. Electrochemical measurements

Corrosion parameters of bare specimen and coatings on brass and bronze substrates were evaluated by potentiodynamic polarization measurements. The calculated data of corrosion parameters of specimens coated with alkaline SiO_2 and HMDS modified SiO_2 prior to and after the artificial ageing are presented in Table 5.

Table 5. Electrochemical data (corrosion rate resistance, R_p, corrosion potential, E_{corr}, and corrosion current, J_{corr}) for uncoated and differently coated bronze and brass substrates before and after the photochemical ageing

No.	Coatings	Corrosion parameters					
		Before photochemical ageing			After photochemical ageing		
		R_p [$\Omega \cdot cm^2$]	E_{corr} [V]	J_{corr} [$\mu A/cm^2$]	R_p [$\Omega \cdot cm^2$]	E_{corr} [V]	J_{corr} [$\mu A/cm^2$]
Bronze							
1.	Uncoated specimen	2425.8	-0.177	0.78	2356.6	-0.176	0.56
2.	3 mas.% SiO_2	687.0	-0.211	4.1	1085.5	-0.195	1.6
3.	Alkaline 3 mas.% SiO_2 with HMDS	1572.9	-0.169	2.9	2047.2	-0.172	0.56
Brass							
4.	Uncoated specimen	1597.1	-0.181	1.98	2061.4	-0.187	7.5
5.	3 mas.% SiO_2	784.4	-0.225	1.2	613.8	-0.234	3.2
6.	Alkaline 3 mas.% SiO_2 with HMDS	1965.24	-0.381	2.3	2297.3	-0.194	0.65

As seen in Table 5, corrosion current (J_{corr}) parameters reveal that resistance to corrosion increased when bare metal specimens are coated with nanosilica coatings. The bare bronze and brass, however, do not correspond to the highest value of corrosion current J_{corr}, respectively 0.78 μA/cm^2 and 1.98 μA/cm^2 prior to artificial ageing. Methyl modified coating possessed the sufficiently low value of corrosion current (2.9 μA/cm^2). Consequently, this coating should protect the surface of bronze from adverse influence. Furthermore, the best properties of brass specimens are noticed for both coatings (3 mas.% SiO_2 – 1.2 μA/cm^2 and HMDS modified silica – 2.3 μA/cm^2). In addition, results of corrosion potential and corrosion rate resistance confirm that the coated copper alloys are better protected than bare samples prior to artificial ageing. Besides, the coated bronze specimens are better protected from adverse influence than brass samples prior to photochemical ageing. In almost all cases, nanosilica modified with HMDS coatings have showed better electrochemical parameters (Bronze: R_p = 2047.2 Ω·cm^2; E_{corr}= -0.172 V; J_{corr} = 0.56 μA/cm^2; Brass: R_p = 2297.3 Ω·cm^2; E_{corr} = -0.194 V; J_{corr} = 0.65 μA/cm^2) in comparison with silica coatings (Bronze: R_p = 1085.5 Ω·cm^2; E_{corr} = -0.195 V; J_{corr} = 1.6 μA/cm^2; Brass: R_p = 613.8 Ω·cm^2; E_{corr} = -0.234 V; J_{corr} = 3.2 μA/cm^2).

CONCLUSIONS

1. Nano SiO_2 was obtained on glass substrate using alkaline and acidic catalytic sol-gel processing. Modification of SiO_2 with trimethylchlorosilane (TMCS) and heksamethyldisilazane (HMDS) in a liquid phase and directly on a surface of coating was developed. It was demonstrated, that modification in a liquid phase indicates better parameters than a direct modification on the surface of SiO_2 coating.
2. It was shown, that SiO_2 obtained by alkaline catalysis has better characteristics than SiO_2 formed by acidic catalysis. Alkaline coatings are more hydrophobic as the value of contact angle was 128.35°–135.92°.
3. Analogous alkaline and acidic catalysis processing were applied for the preparation of protective coatings on copper substrate. FTIR analysis revealed that addition of HMDS decrease the intensity of broad and not intensive band at 3450–3400 cm^{-1} which originates from vibration in –OH group. Part of these groups are changed by $OSi(Me)_3$ groups during the modification of silica with HMDS. Thus it can be concluded that alkaline catalysis and

modification in a liquid phase is more preferable for the conservation of metals.

4. Methyl-modified coatings formed from TMCS and HMDS on copper substrate were distinctly hydrophobic. Moreover, the morphology of coatings modified with HMDS remained unchanged even after the photochemical ageing. However, the growths of aggregates were observed on coatings modified with TMCS. EDS analysis revealed that compounds of chlorine crystallized on the surface.

5. Effective conservation method by forming protective nano SiO_2 and nano SiO_2 modified with HMDS coatings on copper has been developed. HMDS modified coatings showed the best electrochemical data and were slightly affected by the photochemical ageing. However, the value of corrosion rate was sufficient (2830.0 Ωcm^2), corrosion potential is one of the most positive (-0.194 V), and the value of corrosion current is lowest (2.3 μAcm^{-2}).

6. Alkaline catalysis and modification in a liquid phase with HMDS was applied for the conservation of steel. The high contact angle data was observed for the HMDS modified specimen (150.7°). Thus, hydrophobic protective coating was obtained on steel surface. Moreover, the structure of SiO_2 modified with HMDS coating was homogenous.

7. Effective method for the conservation of steel has been developed by obtaining protective coatings of SiO_2 and SiO_2 modified with HMDS. The hydrophobicity was not influenced by photochemical ageing from 14 until 28 days. Electrochemical data showed good quality of coatings obtained after the photochemical ageing (R_p = 1462 Ωcm^2; E_{corr} = –0.024 V; J_{corr} = 2.2 μAcm^{-2}).

8. Alkaline catalysis and SiO_2 modification in a liquid phase with HMDS was applied for the conservation of copper alloys bronze and brass. The value of contact angle increased till ~123 ^{o} after the coating the surface with alkaline SiO_2 modified with HMDS. Obtained coatings were even, homogenous, covered the whole area and remained hydrophobic after the photochemical ageing.

9. Effective conservation method generated for the conservation of copper alloys by forming protective coatings of nano SiO_2 and SiO_2 modified with HMDS on a surface of brass and bronze. The value of corrosion current decrease after coating the samples with modified nano silica coating. The corrosion parameters changed slightly after the photochemical ageing. The best parameters were observed in SiO_2 coatings modified with HMDS: bronze specimen:

R_p = 2047.2 Ω·cm^2; E_{kor}= -0.172 V; j_{kor} = 5.6 ·10^{-6} μA/cm^2; brass specimen: R_p = 2297.3 Ω·cm^2; E_{kor} = -0.194 V; j_{kor} = 6.5 ·10^{-6} μA/cm^2.

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Articles in Journals

1. E. Kielė, J. Lukšėnienė, A. Grigucevičienė, A. Selskis, J. Senvaitienė, R. Ramanauskas, R. Raudonis, A. Kareiva, Methyl–modified hybrid organic-inorganic coatings for the conservation of copper, *Journal of Cultural Heritage* 15 (2014) 242–249.
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Manuscripts in Journals

1. E. Kielė, J. Senvaitienė, A. Griguceviciene, R. Ramanauskas, R. Raudonis, A. Kareiva, Application of sol-gel method for the conservation of copper alloys, *Microchemical Journal*. Submitted (Ms. Ref. No.: MICROC-D-15-00449).

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2. E. Borovikovaitė, J. Lukšėnienė, A. Selskis, J. Senvaitienė, R. Ramanauskas, A. Kareiva. Application of Sol–gel Method for the Conservation of Copper and Steel. International conference “Youth in conservation of cultural heritage – YOCOCU 2012”, Antwerpen, Belgium, June 18–20, 2012.
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NAUJŲ METODŲ METALINIAMS KULTŪROS PAVELDO DIRBINIAMS KONSERVUOTI KŪRIMAS IR TAIKYMAS

SANTRAUKA

Daktaro disertacijoje apibendrintų mokslinių tyrimų tikslas – sukurti naują zolių–gelių metodą metalams ir jų lydiniams konservuoti. Taip pat nustatyti naujo zolių–gelių metodo apsauginėms dangoms formuoti ant stiklo paviršiaus optimalius parametrus. Suformuoti apsaugines modifikuotas silicio dioksido dangas ant vario, vario lydinių ir plieno paviršiaus bei ištirti zolių–gelių metodo tinkamumą metalams konservuoti. Zolių-gelių metodas yra vienas daugiausiai žadančių ir naujausių metodų, kuris gali būti taikomas metalų konservavime. Šiuo metodu gali būti formuojamos hidrofobinės, antikorozinės, apsauginės ir kitos dangos. Apsauginės dangos, suformuotos zolių-gelių metodu, yra chemiškai stabilios ir padidina metalo atsparumą korozijai. Zolių gelių metodas pasaulyje yra plačiai naudojamas akmens, stiklo, keramikos, metalų ir kt. paviršių konservavimui. Lietuvoje zolių gelių metodas kol kas nėra taikomas konservavimo praktikoje. Pirmą kartą SiO_2 dangos panaudotos metalų konservavimui. Optimalūs dangų parametrai nustatyti stiklo paviršiuje. Nustačius optimalius zolių – gelių metodo parametrus stiklo paviršiuje, dangos formuotos vario, vario lydinių (bronzos, žalvario) ir plieno padėklų paviršiuje. 3 % SiO_2 zolio dangos formuotos visų metalų paviršiuje. Vario paviršiuje formuotos bazinės ir rūgštinės katalizės būdu gauto SiO_2 zolio dangos, plieno ir vario lydinių paviršiuje formuotos bazinės katalizės būdu suformuoto SiO_2 zolio dangos. SiO_2 dangų palyginimui suformuotos 6 konservavime naudojamos dangos: 2 % *Plexisol P550–40* acetone, 1 % *Paraloid B 72* etanolyje, 0,5 % PVB etanolyje, 1 % *Paraloid B 67* acetone, 6 % *Cosmolloid H 80* toluene ir 10 % *Antik Patina* vaitspirite. Visos suformuotos

dangos dirbtinai fotochemiškai sendintos. Prieš ir po dirbtinio fotocheminio sendinimo atlikti IR, kontaktinio kampo, AFM, SEM ir EDS, elektrocheminiai matavimai. Tyrimai vario mėginių paviršiuje. Modifikuotos TMCS bei HMDS dangos ant vario padėklo pasižymėjo aukštu hidrofobiškumu. Be to, modifikuotų HMDS dangų morfologija nepasikeičia ir po dirbtinio fotocheminio sendinimo, o modifikuotų TMCS tirpalu vario dangų paviršiuje po sendinimo suintensyvėjo aglomeratų augimas ir kristalitų sankaupos. EDS tyrimai leido padaryti išvadą, kad šiose dangose į paviršių migruoja ir išsikristalina chloro junginiai. Pirmą kartą sukurta efektyvi varinių dirbinių konservavimo metodika formuojant ant jų paviršiaus apsaugines nano silicio oksido, modifikuoto HMDS, dangas. HMDS modifikuotų dangų elektrocheminiai matavimų duomenys po sendinimo išlieka geri, jie pasikeičia nežymiai. Poliarizacinė varža pakankamai didelė (2830,0 Ωcm^2), o korozinis potencialas vienas teigiamiausių (-0,194 V), korozijos srovės vertė maža (2,3 μAcm^{-2}). Plieno paviršiuje zolių–gelių metodu buvo susintetintos nano SiO_2 dangos tik bazinės katalizės būdu ir jos modifikuotos tik metalų paviršiaus neėsdinančiu HMDS. Didžiausios kontaktinių kampų vertės gaunamos zolių–gelių metodu suformuotose SiO_2 dangose, modifikuotose HMDS (150,7°). Taigi, plieno paviršiuje gauta hidrofobiškesnė danga, nei vario paviršiuje. Modifikuoto HMDS silicio oksido dangos mikrostruktūra yra vienalytė. Pirmą kartą sukurta efektyvi plieno dirbinių konservavimo metodika formuojant ant jų paviršiaus apsaugines nano silicio oksido, modifikuoto HMDS, dangas. Dirbtinio sendinimo trukmė nuo 14 iki 28 dienų neturi įtakos padengto plieno paviršiaus hidrofobiškumui. HMDS modifikuotų dangų elektrocheminiai matavimų duomenys po sendinimo išlieka geri, jie pasikeičia nežymiai (R_p = 1462 Ωcm^2; E_{kor} = –0,024 V; j_{kor} = 2,2 μAcm^{-2}). Žalvario ir bronzos paviršiuje zolių–gelių metodu taip pat buvo susintetintos nano SiO_2 dangos tik bazinės katalizės būdu ir jos modifikuotos tik metalų paviršiaus neėsdinančiu HMDS. Po SiO_2 modifikavimo tirpale HMDS tiek bronzos, tiek žalvario padėklų paviršiuje suformuotų dangų kontaktiniai kampai padidėja iki ~123°. Dangos išlieka hidrofobiškos net ir po 28 dienų dirbtinio fotocheminio sendinimo. Dangos ant vario lydinių yra tolygios, nesutrūkinėjusios, jos dengia visą tiriamą bronzos ir žalvario paviršiaus plotą. Pirmą kartą sukurtos efektyvios vario lydinių žalvario ir bronzos konservavimo metodikos formuojant ant jų paviršiaus apsaugines nano silicio oksido, modifikuoto HMDS, dangas. Korozijos srovė sumažėja, kai bronza ir žalvaris padengiami apsauginėmis modifikuotomis nanosilicio dangomis, todėl paviršiaus atsparumas korozijai padidėja. Po dirbtinio fotocheminio sendinimo korozijos parametrai pakito nežymiai. SiO_2 modifikuoto HMDS dangos parametrai beveik visais atvejais išliko geriausi: bronzos mėginio: R_p = 2047,2 Ω·cm^2; E_{kor}= -0,172 V; j_{kor} = 0,56 µA/cm^2; žalvario mėginio: R_p = 2297,3 Ω·cm^2; E_{kor} = -0,194 V; j_{kor} = 0,65 µA/cm^2. Sukurtas zolių–gelių rūgštinės ir bazinės katalizės metodikos nano SiO_2, SiO_2 modifikuotų chlorotrimetilsilanu (TMCS) bei heksametildisilazanu (HMDS) tirpale bei dangos paviršiuje dangoms formuoti ant metalo padėklo. Nustatyta, kad SiO_2 modifikavimas tirpale yra efektyvesnis už tiesioginį modifikavimą dangos paviršiuje. Bazinės katalizės būdu gautas SiO_2 yra tinkamesnis metalui dengti nei gautas rūgštinės katalizės būdu. Bazinės katalizės būdu suformuotos dangos yra hidrofobiškesnės, kurių kontaktinis kampas svyruoja intervale 128,35°–135,92°. Zolių gelių metodas gali būti naudojamas vario, vario lydinių ir plieno konservavimui. Šis metodas yra universalus, gali būti taikomas visiems metalams ir jų lydiniams konservuoti. Kai tuo tarpu dabartinėje konservavimo praktikoje naudojami skirtingi tirpalai, dangos ir metodikos kiekvienam iš metalų konservuoti.