Journal of Cultural Heritage 15 (2014) 242–249

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Original article

Methyl–modified hybrid organic-inorganic coatings for the conservation of copper

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ARTICLE INFO

Article history:
Received 7 February 2013
Accepted 6 June 2013
Available online 10 July 2013

Keywords:
Sol-gel method
Copper
Silica coatings
Dip-coating
Modification
Conservation

ABSTRACT

A simple sol-gel technique for the preparation of methyl–modified silica coatings for the protection of the external surface of copper has been used in this study. Tetraethylorthosilicate (TEOS) has been used as a precursor to prepare nanosilica coatings on the surface of copper. The methyl–modified silica sols were obtained by mixing of 3% SiO_2 sol solution with trimethylchlorosilane (TMCS) or hexamethyldisilozane (HMDS) as basic materials. For comparison, the copper substrates were also coated with commercial polymers (Paraloid B 72, Plexisol P 550-40 and polyvinyl butyral (PVB)). The surface morphology changes of uncoated and coated specimens were investigated by atomic force microscopy (AFM) and scanning electron microscopy (SEM). The hydrophobicity of surfaces and photochemical ageing effects were evaluated by contact angle measurements. Potentiodynamic measurements were obtained in order to compare corrosion parameters of the coatings.

1. Research aims

The aim of this research is to apply sol-gel technique for the conservation of copper and compare physicochemical properties of coatings, obtained from silica with polymeric coatings that are used in conservation of metals.

2. Introduction

The conservation methods of different metals used by conservators and restorators were developed and verified through many centuries. However, the conservation and restoration of metals remains one of the most complex conservation issues. Therefore, a lot of scientific investigations have been made in order to discover new conservation methods that could be used as alternatives to the old ones. These investigations essentially focused on the developing of better quality, faster, long–term, more economical, anticorrosion preservation methods that could be applied in conservation and restoration of metals [1–4]. One of the aims of conservation treatments is avoiding the reactivation of corrosion processes [5]. For example, Bario et al. [2] described the use of electrochemical techniques for the conservation of archaeological metals from Spain. The efficiency of different organic coatings (waxes and resins) for protection of historical steel artefacts was studied by Dumitriu et al. [6]. The protection of metal parts in archaeological iron-wood artefacts was achieved by adding a corrosion inhibitor [7]. This new conservation process, however, was followed by significant microbiological growth. It is known that fungi and bacteria affects a large variety of cultural artefacts including even glass and metals [8,9]. Non-toxic corrosion inhibitors based on carboxylic acids extracted from vegetable oil have been also evaluated for the protection of iron artefacts [10].

Moreover, conservation and restoration procedures had to take into account composition, structure, state of the artefacts, as well as the aesthetic needs, in order to offer some valuable artefacts for the cultural heritage [11–13]. The best way to reduce degradation of metallic cultural heritage is through preventive conservation measures but, in many cases, it is not possible to obtain adequate environmental conditions [14–18], and it is necessary to apply coatings to the artefacts in order to protect them against corrosion.

The sol-gel process is an efficient method for producing coatings with different chemical compositions on a variety of substrates and having important industrial applications (fibres, aerogels etc.) [19]. Hydrophobic, anticorrosion, self-cleaning and other coatings can be formed by sol-gel method [20–24]. Sol-gel protective coatings have shown excellent chemical stability, oxidation control and enhanced corrosion resistance to different substrates [25–30]. Moreover, the sol-gel method is an environmentally friendly technique for the

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http://dx.doi.org/10.1016/j.culher.2013.06.002

protection of surfaces and had showed the potential for the replacement of toxic pre-treatments and coatings which have traditionally been used for increasing corrosion resistance of metals [31–35].

Despite copper ions are acting as biocides [36], the copper-based artefacts surface is dramatically affected by different insoluble corrosion products like AgCl, Ag_2S, CuS, AgCuS, Cu_2O or copper carbonates [37]. However, the sol-gel technique is not used widely for the preservation of copper artefacts so far. Bongiorno et al. [38], Franceschi et al. [39] and Farme et al. [40] contributed to the improvement of restoration and conservation sciences investigating artificial and natural patinas of copper-based alloys using micro-Raman spectroscopy and other techniques. The conservation method based on transformation of existing corrosion patinas on outdoor bronze monuments into copper oxalates has been suggested [41]. However, this method allows to preserve the physical appearance of these artefacts only for short time even the copper oxalate shows a high degree of insolubility and chemical stability even in acidic atmosphere. The effectiveness of corrosion inhibitor films for the conservation of bronzes and gilded bronzes have been also investigated [42]. The silica based coatings, prepared by a single step sol-gel process using methyltriethoxysilane as a precursor was found to be attractive anticorrosion coatings for copper surface [34].

In the present study, a sol-gel processing route has been developed for the preparation of the protective coatings for copper. Numbers of silica hybrid coatings on copper substrates were prepared using dip-coating technique. The methyl groups were selected as silica modifiers to increase the hydrophobicity, and consequently, the protective ability of the coatings. In order to compare the efficiency of proposed sol-gel method, the copper substrates were also coated with polymers (Paraloid B 72, Plexisol P 550-40 and polyvinyl butyral (PVB)). The hydrophobicity of obtained coatings was evaluated by contact angle measurements. The morphological features of just obtained and photochemical aged coatings on the metallic copper were determined by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The corrosion parameters were obtained by potentiodynamic polarization measurements.

3. Experimental

3.1. Preparation of sols and solutions

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. 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 the hydrolysis, the 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, the 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. In the route 1, the modification of colloidal nanosilica was performed in liquid phase following the dip-coating of copper substrates. During route 2, the obtained silica coatings on copper substrates were treated with TMCS and HMDS solutions. So, the silica coated copper surface was modified. The schematical diagram of the preparation of coatings on copper surface is presented in Fig. 1. As seen, eight differently prepared coatings were formed by sol-gel method on copper substrates.

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) 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 and 0.5 mass% PVB in ethanol. Solutions were aged at a room temperature for 2 days.

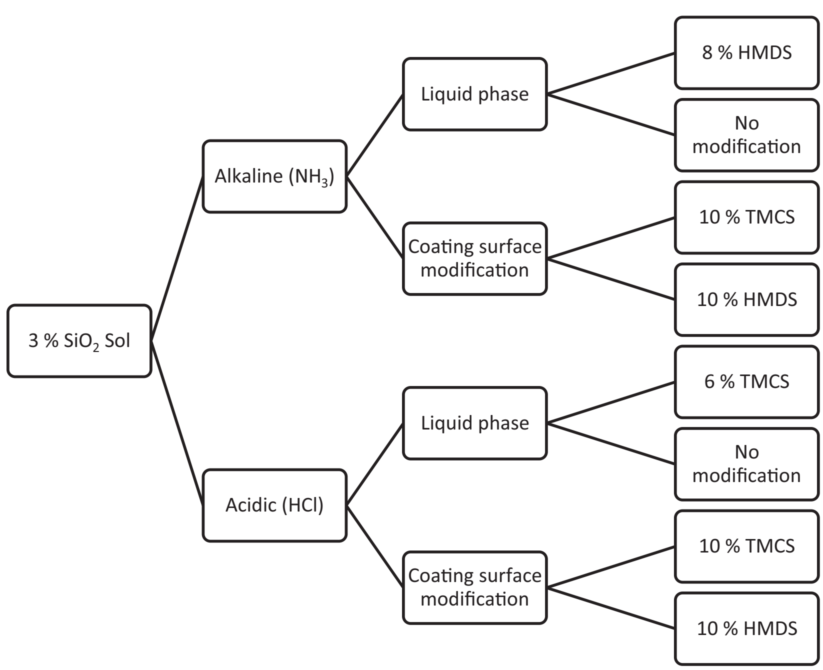

Fig. 1. The chart of synthesis and formation of the coatings by sol-gel method using two different routes: modification in liquid phase and modification of silica coated surface.

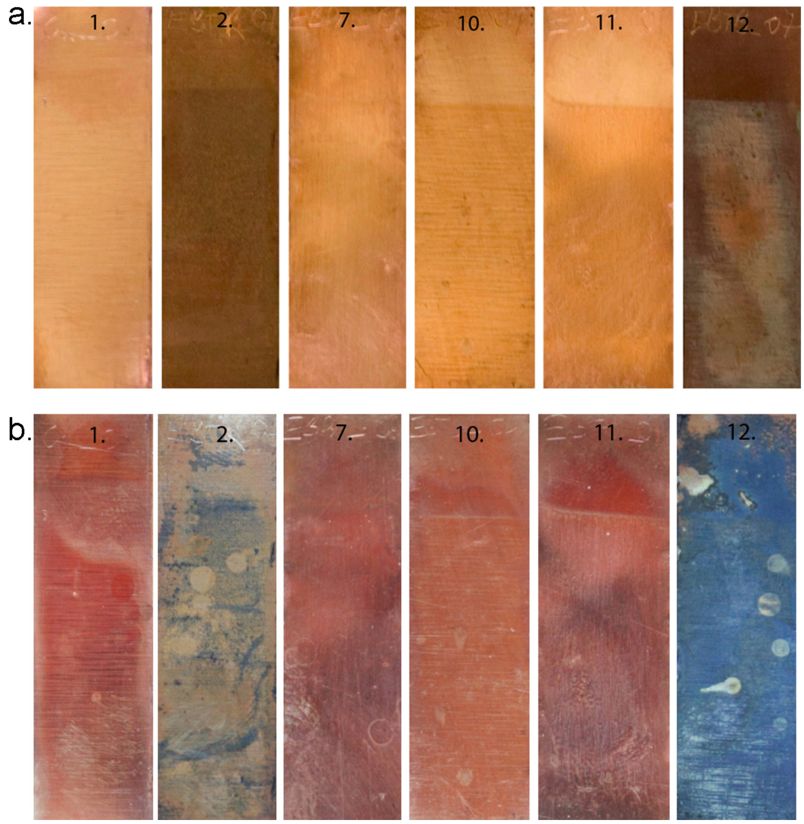

Fig. 2. Photos of copper plates coated with different coatings before (a.) and after (b.) photochemical aging. Number of specimens represents the number of the coating conditions in Table 1.

3.2. Preparation of films

Different protective coatings were deposited on copper plates (1.7×5.0 cm) which had been cleaned with 1% sulphuric acid, mechanically treated with steel wool and then washed with ethanol. The dip-coating technique was used to prepare the coatings on the copper substrate. The dip-coating process was performed by immersing the pre-treated copper substrate into the sol-gel or polymeric solution and followed by withdrawal of the pre-treated metal substrate from the solution. The speed of immersion was 85 mm/min. The specimen retained in the sol-gel solution for 20 s and withdrawal was followed by the speed of 40 mm/min. The process was performed in a constant temperature and atmosphere in a laminar box.

3.3. Characterization

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. Optical subsystem was used to capture the profile of pure liquid on a solid substrate. Atomic force microscopy (AFM, Bioscope II, Veeco) was used to obtain topographic images and investigate the morphology of the samples. EVO 50 EP (Carl Zeiss SMT) 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 $E^{\circ}Ag/AgCl = 0.197$ V. Electrochemical parameters were obtained: j_{corr} – corrosion current, E_{corr} – corrosion potential, R_p – corrosion rate resistance. 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.

3.4. Artificial ageing

The 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 samples were placed about 0.5 m below the lamps. The temperature in the reactor was 40 °C and relative humidity was 17%. The samples had been aged for 14 days.

4. Results and discussions

4.1. Contact angle measurements

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 [37,43]. 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 during the process of photochemical ageing. The photos of representative copper plates covered with protecting layers before and after photochemical ageing are shown in Fig. 2. According to visual observation, the photochemical aging had a negative impact on the surface of conservated copper. However, the seriousness of influence could be determined only after physicochemical

Table 1
The contact angles determined on different copper surfaces before and after photochemical aging with standard deviations within parenthesis.

No.	Coating conditions	Before aging	After aging for 14 days
1.	Cleaned uncoated copper surface	78.8 (5)	83.0 (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)

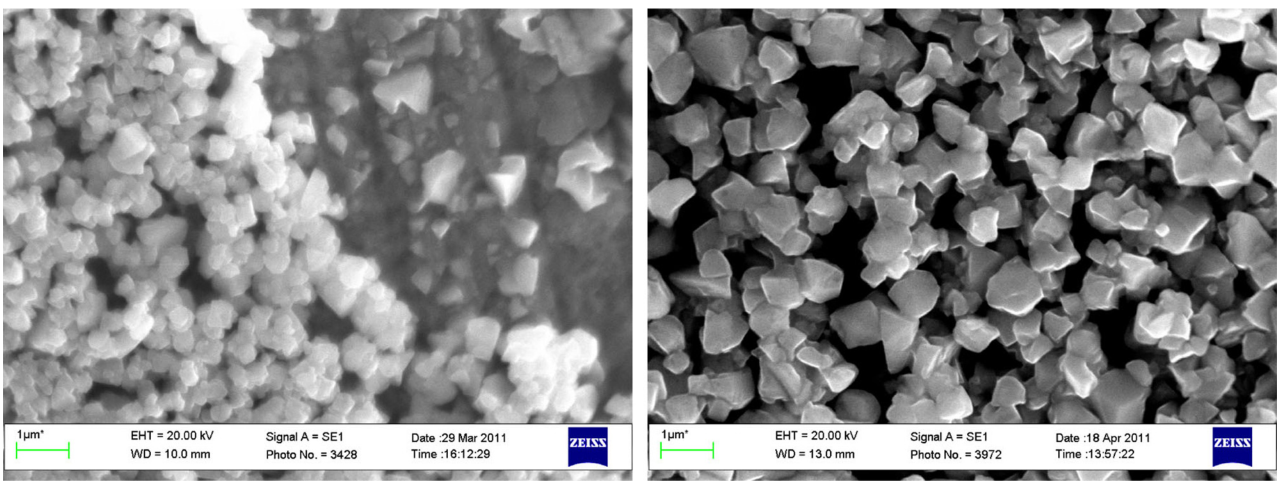

Fig. 3. SEM micrographs of coatings (alkaline; route 2; with 10% TMCS) before (left) and after (right) photochemical aging.

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°. Moreover, the contact angle of non-modified silica surface was 69.5°. These results clearly demonstrate that the modification of silica with TMCS on the surface does not proceed when silica was obtained by acidic catalysis. Very similar results were obtained when modification at the same conditions was performed with HMDS. However, the exact reasons for this phenomenon are not clear and should be determined in future. On the other hand, acidic 3% SiO_2 modification in liquid phase with 6% TMCS produced coatings with contact angle of 113.5°, which was higher than that of 78.8° of the uncoated copper substrate. Recently, the possible modification of silica with TMCS in solution using acid catalyzed silica sols was demonstrated elsewhere [44].

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° 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 [45,46]. When silica surfaces were modified in a liquid phase with 8% HMDS, the determined contact angle was 132.7°. The modification of nanosilica coating obtained also from alkaline media with 10% TMCS immediately on the surface gave contact angle value of 135.9°. 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°) even after ageing. This could be clearly illustrated by the change of water droplet placed on the coating. Can trimethylchlorosilane sustain artificial

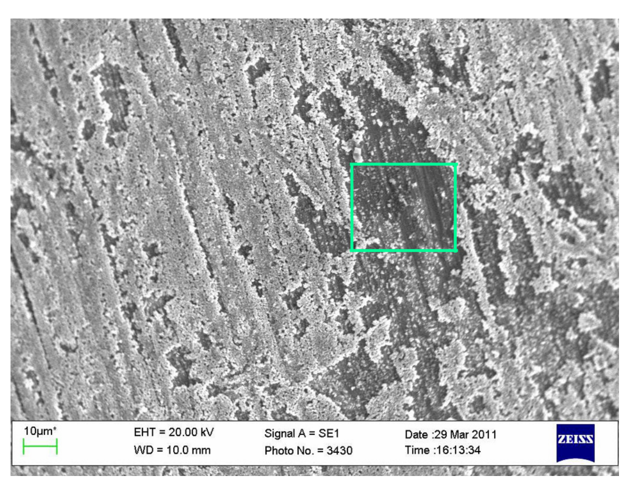

Fig. 4. SEM micrograph of coating (alkaline; route 2; with 10% TMCS) before photochemical aging obtained at lower magnification.

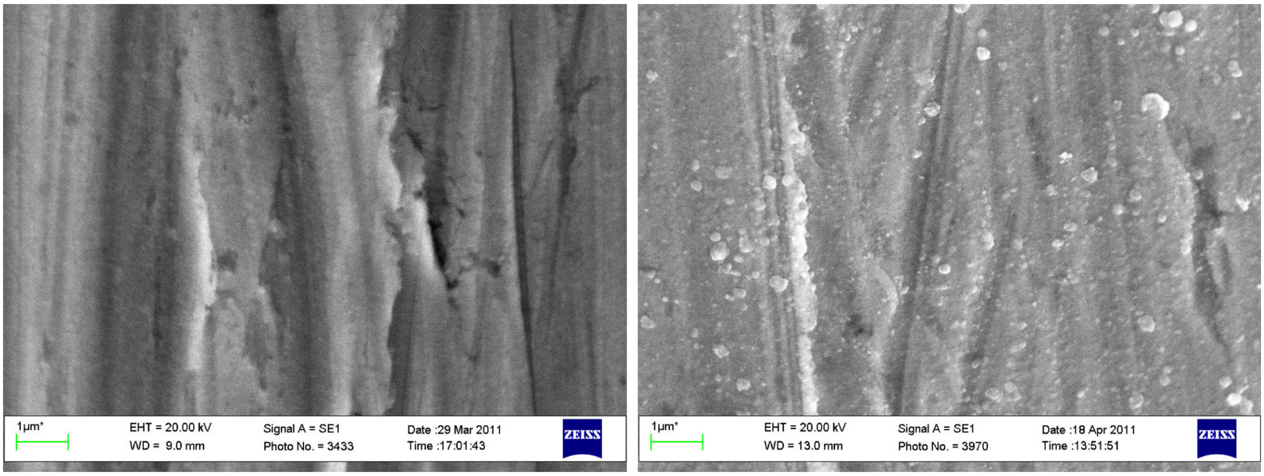

Fig. 5. SEM micrographs of coatings (alkaline; route 1; with 8% HMDS) before (left) and after (right) photochemical aging.

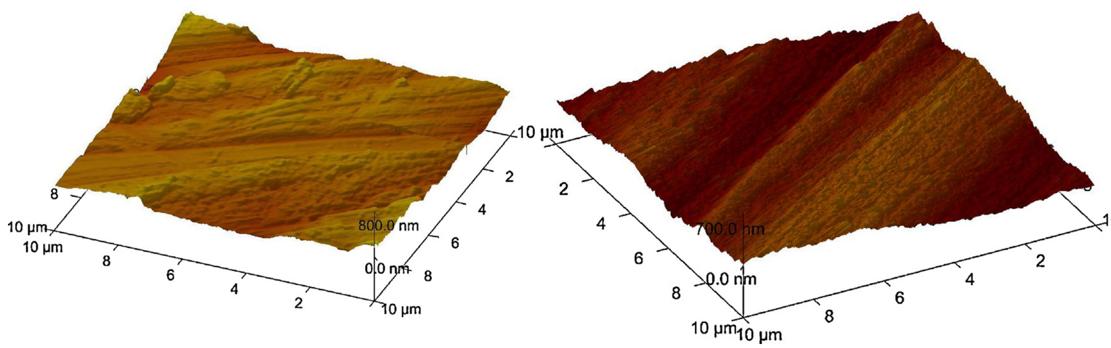

Fig. 6. AFM micrographs of cleaned copper surface before (left) and after (right) photochemical aging.

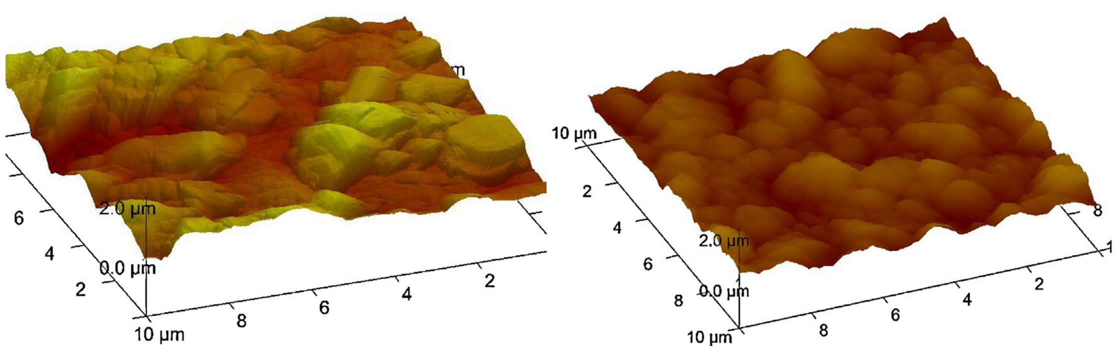

Fig. 7. AFM micrographs of coatings (alkaline; route 2; with 10% TMCS) before (left) and after (right) photochemical aging.

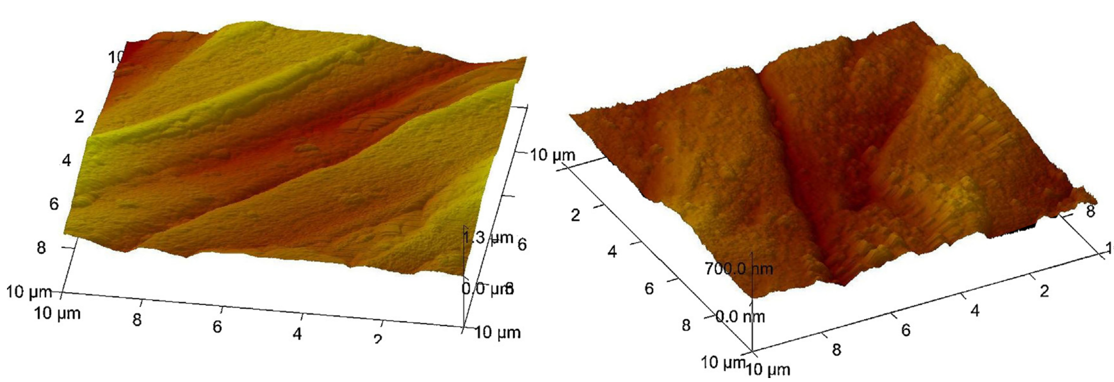

Fig. 8. AFM micrographs of coatings (alkaline; route 1; with 8% HMDS) before (left) and after (right) photochemical ageing.

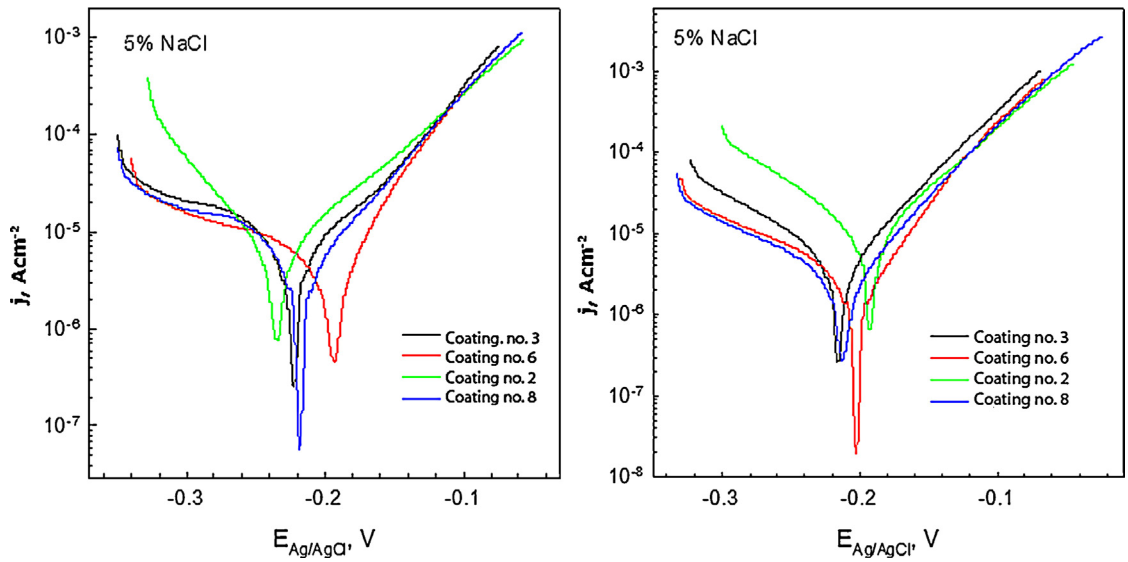

Fig. 9. Polarization curves of acidic modified SiO_2 films on copper substrates before (left) and after (right) photochemical aging.

ageing conditions more effectively than hexamethyldisilozane, or the changes of contact angle of these hybrid organic-inorganic coatings on ageing are affected by external parameters (temperature, relative humidity, duration), the question will be answered in the following chapters.

Thus, the results obtained by contact angle measurements [47] 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.

4.2. Scanning electron microscopy

The morphological analysis of the obtained film surfaces was performed by SEM analysis. Fig. 3 presents the SEM images of the SiO_2 coating prepared using alkaline conditions and modified with 10% TMCS (route 2). The surface of TMCS modified films consists of particles of different shape less than 1 μm in size. As seen from Fig. 3, 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; route 2; with 10% TMCS) before photochemical ageing and obtained at lower magnification is presented in Fig. 4. The area where the concentration of chlorine was the highest is marked.

The SEM micrographs of the SiO_2 coatings prepared using alkaline conditions and modified with 8% HMDS (route 1) are shown in Fig. 5. Fig. 5 clearly demonstrates that the surface microstructure of HMDS modified film differs significantly from that of presented in Figs. 3 and 4. The films show a smooth and uniform surface with regular morphology. The formation of nonporous surface microstructure [48] 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

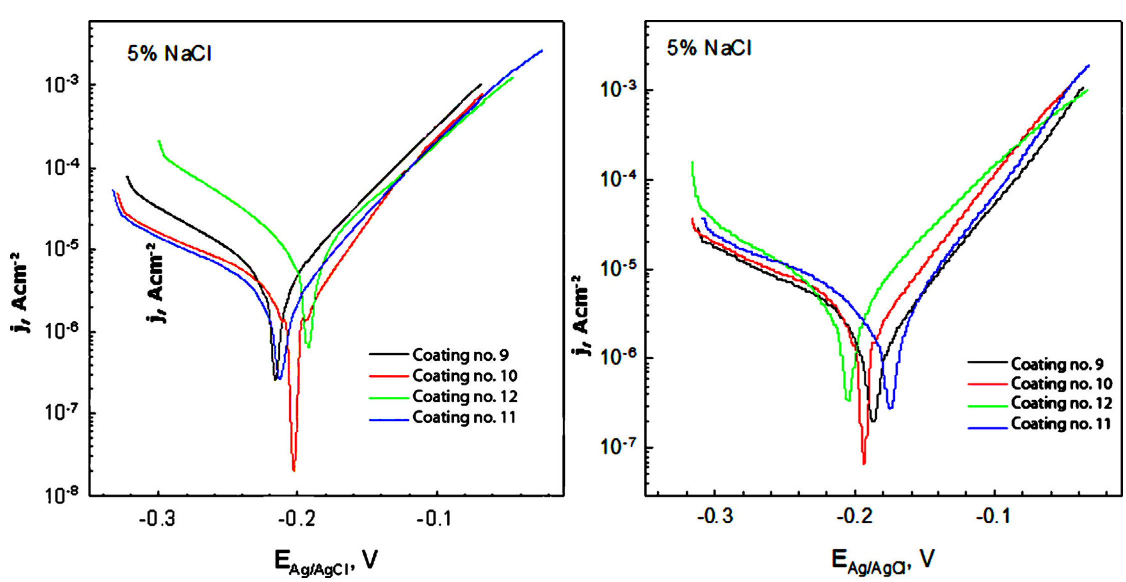

Fig. 10. Polarization curves of alkaline modified SiO_2 films on copper substrates before (left) and after (right) photochemical aging.

analysis results showed that there is no chlorine apart expected elements (C, O, Si, Cu).

4.3. Atomic force microscopy

Three-dimensional topographic AFM images of copper specimens obtained at different coating conditions are shown in Figs. 6–8. Clearly, the surface of as prepared copper plates is not very smooth and probably had been scratched during the cleaning process (Fig. 6). The root mean square roughness (Rms) of the surface reached about 100.5 nm in the scanning field. Evidently, negligible changes in surface morphology were observed after artificial aging of copper sample for 14 days. The AFM images of SiO_2 coating prepared using alkaline conditions and modified with 10% TMCS on the surface of the coating (route 2) are shown in Fig. 7. The roughness of the surface obtained by modification with TMCS increased significantly [49]. RMS roughness values of determined by AFM were ~145 nm. Besides, the islands appeared [50] 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 (route 1) are shown in Fig. 8. The SiO_2 coatings modified in the liquid phase with 8% HMDS are sufficiently even and smooth. However, the surface roughness again was very high. 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.

4.4. 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 Figs. 9 and 10, respectively.

It was determined that coatings modified with HMDS showed better corrosion parameters (R_p = 2796.8 cm^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 cm^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.

5. Conclusions

The simple sol-gel technique for the preparation of methyl–modified silica coatings for the conservation of copper was suggested. Tetraethylorthosilicate (TEOS) has been used as a precursor to prepare nanosilica films on the surface of copper. The methyl–modified silica coatings were obtained using trimethylchlorosilane (TMCS) and hexamethyldisilozane (HMDS) as modifying agents. It was demonstrated that alkaline conditions are more preferable for the preparation of the more stable and hydrophobic coatings. The contact angle of copper surface (78.8°) was significantly lower than that of silica films modified with HMDS (132.7°) and TMCS (135.9°). The silica coatings with HMDS were sufficiently even, smooth and uniform with regular morphology. However, the surface of TMCS modified films was rough and consisted of submicrosized particles of different shape. On the other hand, the degradation of hydrophobic properties of surfaces of all coatings after photochemical aging was observed. The potentiodynamic polarization measurements confirmed that HMDS is suitable as silica modification agent for coatings on copper substrate since the surface of the copper was not affected by corrosion. Therefore, we can conclude that protective HMDS modified silica coatings on copper substrate could be successfully used for the conservation of copper at ambient conditions.

Acknowledgment

This research was funded by the Research Council of Lithuania grant (No. TAP LU 04/2012) and COST Action MP1202.

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