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# Application of sol–gel method for the conservation of copper alloys☆

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ABSTRACT

In the present study, $SiO_2$ coatings are presented as an alternative to the traditional ones, used in conservation of metals. The preparation of methyl–modified nanosilica coatings by the sol–gel technique to protect the external surface of copper alloys is discussed herein. The methyl–modified silica sols were obtained by mixing of 3% $SiO_2$ sol solution with hexamethyldisilozane (HMDS). The surface of brass and bronze specimens was coated by dip-coating technique. The structural features of the coatings were evaluated by FTIR spectroscopy. The hydrophobicity of the surfaces was investigated by contact angle measurements. The surface morphology changes of bare and coated specimens prior and after photochemical ageing were evaluated by atomic force microscopy (AFM) and scanning electron microscopy (SEM). Potentiodynamic measurements were obtained in order to compare corrosion parameters of the coatings.



## 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 minimum change to an object while achieving this and restoration to the former state is rarely carried out [1]. While preservation appears to be a straightforward 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 [2]. Research into the corrosion and conservation of historic and archaeological metals is developing significantly [3,4] due to the increasing contribution of dedicated specialists that have a specific focus [5,6] and the challenges of large complex objects.

Available in several forms, bronze and brass were commonly employed in cultural heritage objects. Since these alloys are easily shaped and have special corrosion properties, they were commonly used in cultural heritage objects such as sculptures, other outdoor decorative items, swords, details of appearing, jewelry, etc. [7–9]. Corrosion inhibitors, polymer and synthetic wax coatings are used for the conservation of bronze and brass objects [3,4,6,10–13]. However, these methods do not provide successful preservation of copper alloys 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 [14–16].

Sol–gel derived coatings have already been applied for surface protection of metal specimens [16,17]. However, the properties of the coatings may diverge on different metal substrates. Namely, sol–gel method is highly perspective for obtaining thin [18], 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. [19].

In this study, the sol–gel technique was suggested for the fabrication of protective coatings for bronze and brass. For this purpose, silica-based and silica-based methyl–modified coatings have been prepared. Sol–gel-derived coatings were obtained from tetraethylorthosilicate (TMCS) using a dip-coating process. Hexamethyldisilozane (HMDS) was used for methyl modification of silica to increase protective and hydrophobic properties of the coating. Coated bronze and brass substrates were photochemically aged. Although the copper case has previously been studied [17], this paper describes additional research of bronze and brass specimens.

## 2. Experimental

### 2.1. Preparation of sols

The colloidal silica sols were prepared using tetraethylorthosilicate (TEOS; Fluka, ≥98%) as a starting material. Three percent $SiO_2$ was obtained by alkaline catalysis using ethanol (EtOH) as a solvent and $NH_3$

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as a catalyst. The molar ratio of components during alkaline catalysis was TEOS:$NH_3$:$H_2O$:EtOH = 1:0.2:2.97:34.72. $SiO_2$ sol was aged for 19 days at 25 °C to complete hydrolysis. The modification of colloidal nanosilica was performed by adding hexamethyldisilozane (HMDS; Sigma Aldrich, ≥98%) to the prepared alkaline sol. Alkaline and methyl–modified sols were used to attain the coatings on bronze and brass substrates.

### 2.2. Preparation of films

Bronze (Cu 89.0–91.0%; Sn – remainder) and brass (Cu 68.5–71.5%; Zn – remainder) substrates (1 × 1.5 cm, 1 mm thick bronze and brass foil, Alfa Aesar) were treated mechanically with aluminum oxide paper and then washed with ethanol. Alkaline and methyl–modified coatings were deposited on bronze and brass specimens by the dip-coating process: pre-treated brass and bronze substrate was immersed into the sol 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.

### 2.3. Artificial ageing

Sol–gel derived 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 45 °C, relative humidity – 19%. The samples had been aged for 28 days.

### 2.4. Characterization

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 FTIR 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. 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. Contact angle measurements

Bare, coated bronze and brass specimens were aged in a photochemical reactor under the conditions described in the Experimental section. Periodic contact angle measurements and photo-fixation have been performed. Regarding to visual observations (color, 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 1. Table 1 indicates that contact angle value of bare bronze specimen is comparatively high – 105.42°. However, during the artificial ageing it decreases until 95.14°. The bronze remains, however, hydrophobic enough as it is noted that hydrophobic surface is at least of 95° [20]. Interestingly, brass is less hydrophobic as the contact angle value of bare brass is 94.29° and decreases 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 [21]. The value decreases gradually during the photochemical ageing and reaches 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. The images of water drop on bronze and brass surfaces coated with nanosilica modified with HMDS are presented in Fig. 1.

**Table 1**
The contact angles determined on uncoated and differently coated bronze and brass specimens before and after photochemical ageing.

| No. | Coating conditions | Contact angle [°] | | |
|---|---|---|---|---|
| | | Before ageing | After ageing for 14 days | After ageing 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) |

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 [22]. To compare, the 2% Plexisol P 550-40 coating on copper substrate before the photochemical ageing is hydrophobic (95.6°) but decreases until 68.8° after the artificial ageing [17]. 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 do keep at least 120° after the artificial ageing.

### 3.2. Atomic force and scanning electron microscopy

Atomic force microscopy observations revealed that the surfaces of bare specimens are rough (Fig. 2). 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. 2). The root mean square roughness (RMS) of the surface reached about 105 nm in the scanning field. Notably, artificial ageing slightly affected the surface of the coatings: brass and bronze surfaces became a bit rougher (Fig. 3). RMS roughness values of determined by AFM were ~145–150 nm. This observation might indicate that after the photochemical ageing the coatings remain thinner. Moreover, rougher surface gives a higher contact angle value.

SEM analysis was performed to inquire morphological characteristics of the bare and coated metal samples prior to and after the photochemical ageing (see Fig. 4). Apparently, observed differently oriented lines and traces are originated from the surface preparation and cleaning procedure, i.e. polishing the bronze and brass with aluminum