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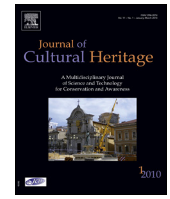

Original article

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

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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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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.

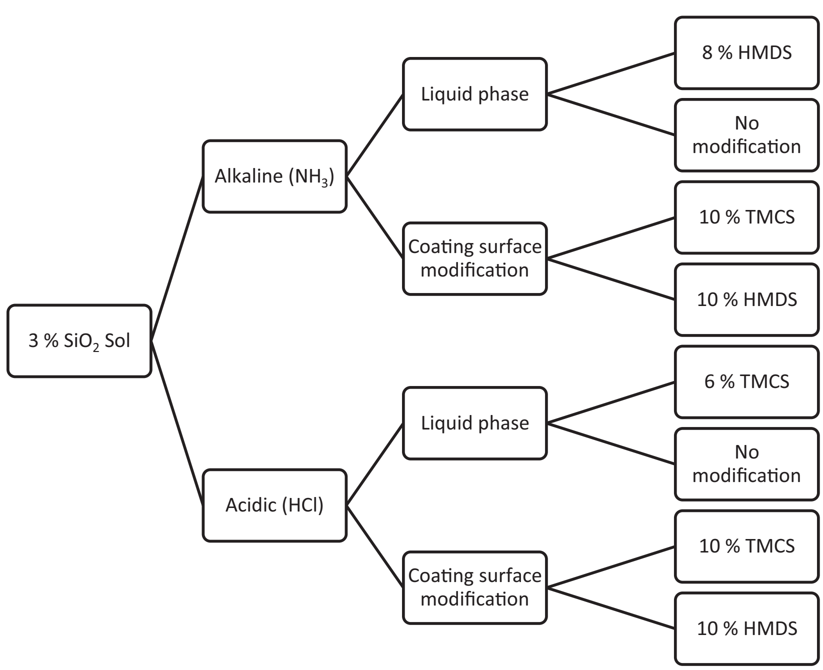

Fig. 1. The chart of synthesis and formation of the coatings by sol-gel method using two different routes: modification in liquid phase and modification of silica coated surface.