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Smart conservation methodology for the preservation of copper-based objects against the hazardous corrosion

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ABSTRACT

"Bronze disease" is a very dangerous cyclic copper corrosion phenomenon which commonly develops after the discovery of the artefact. Therefore, in the cultural heritage field every object is inimitable and whatever loss is irreplaceable, causing a protective coating to be indispensable. Herein we studied the efficiency of a transparent, protective and reversible diamond-like carbon (DLC) coating, deposited by plasma enhanced chemical vapour deposition on copper based alloys, to enhance the corrosion resistance of archaeological artefacts. The nanostructured DLC film resulted in the formation of a structure that exhibits water repellent properties and can act as a barrier layer to corrosion. Exposure of copper based alloys, with and without the DLC coating, to an aggressive chemical environment led to a remarkable inhibition of corrosion only for the coated samples. Moreover the DLC film on the Cu-based substrate was shown to have no effect on the morphology of the surfaces indicating that surface appearance is not affected. Consequently DLC coatings open a pathway into the development of safe and tailored solutions in the ancient metals conservation field. Furthermore the use of DLC coatings can be extended for the protection of objects that do not belong to cultural heritage but may still be subject to corrosion.

1. Introduction

The conservation of ancient metals is critical due to the complex nature of the artefacts (chemical composition and metallurgical features of the artefacts) and of the corrosion products. In particular, archaeological metallic objects are affected by dangerous post burial corrosion phenomena that can damage their original surfaces. Specific compounds, such as reactive cuprous chloride, may grow the artefact's surface after exposure to the atmosphere, via interaction between the copper of the alloy and the chloride ions coming from the soil during the burial, giving rise to the development of further degradation processes. Therefore the study of innovative materials and methods for the conservation of archaeological metallic artefacts is essential to ensure the long lasting protection of the ancient objects. New solutions for a reliable conservation of metallic artefacts and innovative materials and tailored methods able to stop, definitively, the dangerous post-burial corrosion phenomenon that affects the chemical-physical stability of the ancient metals are urgently sought [1–8]. Moreover strategies and the materials able to prevent the exposure of the alloy to external corrosive agents should be as least invasive as possible in order to preserve the artefact [9].

One of the alloys most commonly used in the past was bronze. From a conservation point of view, the results of a chemical investigation on several bronze artefacts coming from different archaeological sites showed that the most aggressive corrosion agent for Cu-based artefacts is chlorine (Cl^-) that, generally, forms cuprous chloride (nantokite, CuCl) via the interaction between copper and Cl^- anions coming from the soil, at the interface between the external patina and the surviving metal [10]. The exposure of reactive cuprous chloride species to the atmospheric moisture and oxygen induces the development of a continuous process of dissolution of copper, "bronze disease", which is very dangerous for the chemical-physical stability of the copper-based artefacts. When cuprous chloride is exposed to the atmospheric humidity, it cyclically reacts with the oxygen and the water coming from the surrounding environment, thus giving rise to the formation of the greenish atacamite and its polymorphs [$2Cu_2(OH)3Cl$] that, in turn, reacts with copper to form new cuprous chloride and water. In this way copper, chlorine, oxygen and water are converted into cuprite [Cu_2O] and atacamite [$2Cu_2(OH)_3Cl$] in a cyclical and continuous process that can disfigure the archaeological objects [11–22]. Strategies to avoid degradation imply the use of show cases in controlled atmosphere to protect ancient metals or the application of coatings able to isolate the surface of the artefacts from the surrounding environment, avoiding further corrosion reactions. Usually, inhibiting materials, such as organic resins, combined with waxes are used for sealing and preserving the artefacts during the traditional conservation treatments, however, they are subject to degradation over time.

The possibility to produce nano-structured films that increase the hydrophobicity of the surface isolating it from the surrounding

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environment, has been suggested as a potential approach for the surface protection of Cultural Heritage assets [7,9,23–27]. As a matter of fact, most of the current studies show that the surface properties of materials, such as wettability behaviour, are related to the chemistry and the micro- and nano-scale topography of the surface [7,28]. Plasma treatments allow deposition of thin nano-structured films able to modify some surface properties depending on the characteristic of the film produced. In particular, Plasma Enhanced Chemical Vapour Deposition (PECVD) of thin Diamond-Like Carbon (DLC) films can modify some surface properties of the bronzes, such as the water repellency, influencing their corrosion resistance. In fact DLC film properties such as high hardness, high electrical resistivity, low IR absorption, transparency to visible light and chemical inertness have proved to have many important advantages in several applications as in water repellent coatings and in the field of conservation of metallic artefacts [23,29–32]. Furthermore DLC coatings allow to tune conveniently the properties of the surface affected by sp^2/sp^3 ratio and hydrogen content, by selecting properly the deposition parameters [33–36]. Therefore it is possible to produce tailored transparent, reversible and protective coatings to apply in the Cultural Heritage safeguard field [9,27].

In the work presented here, we investigate the protective properties and the water repellency behaviour of the DLC coatings on Cu-based alloys, designed to reproduce the properties of the ancient bronze alloys as close as possible [37]. The analytical approach was mainly based on microscopy and spectroscopy techniques to identify the effectiveness of the coating and identify the corrosion products. We show that the aesthetic appearance of the artefact was preserved due to the thinness and transparency of the coating. We also verified the effective reduction of the copper degradation processes on the treated surfaces simulating a highly corrosive ambient and characterizing the degradation of the coating. Additionally the reversibility of the DLC film was evaluated, according to conservation requirements. Techniques used included XRD, Raman, contact angle, SEM–EDS and AFM. Our results provide a promising technique for the protection to the ancient artefacts through nanocoating of low surface free energy DLC materials that act as barrier layer improving archaeological bronzes corrosion resistance. Also the use of hydrophobic DLC coatings can be extended for the protection of bronze objects as predictive corrosion control strategies in marine contexts.

2. Experimental details

2.1. Sample preparation

Cu-based reference alloys [Cu 92.8 wt%, Sn 6.8 wt%, Pb 0.2 wt%, S 0.2 wt%] with a chemical composition and metallurgical properties representative to those of the ancient alloys have been chosen for investigation of corrosion effects [37]. Surface finishing of the reference alloy was performed to obtain a surface that mimics culture heritage objects.

The DLC films were deposited via PECVD with a capacitively coupled asymmetric plasma reactor, driven by 13.56 MHz radio frequency (RF) power supply connected to the upper electrode. Other experimental details on the employed PECVD technique were reported elsewhere [27,38]. DLC deposition was carried out through PECVD in CH_4/Ar atmosphere (40 sccm/50 sccm) by applying 50 W of RF power and maintaining the substrate temperature at 300 K. The Cu-based alloys were placed on the grounded electrode (anode). The starting pressure in the chamber was about 10^{-6} mbar, whereas the total working pressure was dependent on the gas flow, i.e. around 10^{-1} mbar. All the gases, used for the deposition, were of purity degree 5.0. The deposition time was 120 min, corresponding to a film thickness of about 200 nm.

2.2. Plasma treatment

Etching treatments were performed with the same equipment used for the plasma deposition, using an oxygen plasma (10 sccm), placing the samples at the electrically powered electrode, power 50 W with a pressure of $1.6 \cdot 10^{-1}$ mbar and varying different exposure of etching time (1–35 min).

2.3. Degradation test

To test the corrosion inhibiting properties of the DLC coating, an accelerated degradation procedure was developed. The unprotected and the DLC-coated alloys were exposed to an acid atmosphere (HCl 0.1 M aqueous solution) in a sealed glass placed in an electrically heated stove, in highly aggressive conditions (RH 100%, T 50 °C, time 2 h).

2.4. Characterization measurements

SEM-EDS characterization was carried out by using a Cambridge 360 scanning electron microscope equipped with a LaB_6 filament coupled with an energy dispersive (EDS) X-ray spectrometer INCA 250 and a four-sectors back-scattered electron detector (BSD). Samples were coated with a thin layer of carbon in order to avoid charging effects.

Structural identification of crystalline phases formed on the surface of the degraded bronze alloys was determined by a Siemens 5000 X-ray powder diffractometer using a Ni-filtered Cu Kα radiation ($\lambda = 1.5418$ Å). Angular values in the range between 10° and 80° in additive mode, a step size of 0.05° and a sampling time of 2 s are the experimental parameters used for data acquisition. In order to identify the crystalline species X-ray diffraction patterns analysis were carried out by using electronic databases.

AFM imaging was performed on a Multimode 8 microscope equipped with a Nanoscope V controller and a type E piezoelectric scanner (Bruker, USA). Samples were scanned in air using Peak Force Tapping mode with Scanasyst-Air probes (Bruker, USA) at a scan rate of 0.5 Hz. Raw images were fitted with a first order plane and measured to obtain surface roughness parameters using Gwyddion v2 [39].

Water contact angle (WCAs) measurements were carried out using deionised water in atmosphere at room temperature and using the sessile drop method of a contact angle goniometer (Dataphysics OCA 20, Germany). A drop of 3 μL was deposited on the surface, and each reported angle was calculated as the average of six measurements in different points on the sample. The contact angle hysteresis was calculated by the dynamic sessile drop method where the droplet was placed on a horizontal surface. The advancing/receding contact angle was the maximum/minimum angle measured whereas the volume of the droplet was increased/decreased without increasing/decreasing the solid-liquid interfacial area.

Tilt angle measurements were carried out using a tilt table plate with a fixed inclination angle varying from 0 to90°, to which the sample was fixed. A drop of 5 μL was applied to the Cu-based alloy, and the plate was slowly inclined until the drop started to move. Contact angle measurements were carried out also to evaluate surface energies (SFE) using water as the polar liquid and diiodomethane as the apolar liquid.

The surface free energy (SFE) was calculated by applying the Owens-Wendt-Rath-Kaeble (OWRK) method, also referred to as geometric mean [35].

Raman measurements were performed with a Renishaw spectrometer equipped with a cooled CCD detector in conjunction with a Leica microscope. A 100× objective was used to focus the laser light on the samples and to collect the Raman signal. The excitation light was the 514.5 nm line of an argon ion laser.

The surface morphology of the reference Cu-based alloys was observed using a Leica MZ FLIII optical microscope and a Leica Multi-Focus optical microscope (OM) equipped with a digital camera.

3. Results and discussion

A guiding tenet in Cultural Heritage is the preservation of the aesthetic appearance of ancient objects. This is a challenging concept due