



Indoor environmental corrosion of Ag-based alloys in the Egyptian Museum (Cairo, Egypt)



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ABSTRACT

In this study, we have investigated the indoor environmental corrosion of Ag-based alloys after long-term exposure in a showcase of an exhibition room and in the open atmosphere at the Egyptian Museum of Cairo (Egypt). In order to simulate the corrosion processes that occur at the surface of archaeological artefacts, Ag-based alloys with chemical composition, metallurgical features and micro-chemical structure similar to those of ancient alloys have been purposely produced as sacrificial reference samples. Our findings show that corrosion phenomena on alloy surface are mainly caused by environmental sulphur and chlorine containing species that react in different ways depending on the exhibition conditions and on the alloy composition. This approach allows to identify the degradation agents and mechanisms that really take place at the surface of objects similar to ancient artefacts without the necessity of sampling them. Moreover, it is possible to get useful indications for the safe storage or exhibition of silver archaeological artefacts, their cleaning and conservation.

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1. Introduction

The reliable conservation and safe valorisation of cultural heritage is an essential mission and a fundamental responsibility of the Mediterranean Countries where most of the ancient and fascinating witnesses of human art and creativity are conserved. A significant part of this cultural heritage consists of metal artefacts that are often exposed to the harmful and long-term effects of environmental degradation, inappropriate handling and intrinsic chemico-physical instability [1–4]. Furthermore, archaeological metal artefacts often suffer critical conservation problems also due to post-burial corrosion phenomena that may occur during storage and exhibition. These phenomena are mainly related to high relative humidity (RH) and aggressive agents present in the atmosphere that could induce or accelerate the degradation processes [1–11]. The risks can be mitigated if there is a proper knowledge of

the occurring phenomena and adequate materials and methods to counteract deterioration processes [1–18].

A relevant issue for the reliable and safe conservation of museum metal artefact collections is the monitoring of the atmospheric corrosion aimed to detect reactive species such as Cl^- , H_2S , carbonyl sulphide (OCS), SO_2 , CO_2 , NO_x , O_3 or organic or inorganic corrosive compounds in the open atmosphere, showcases and store boxes where precious archaeological artefacts are exhibited or stored [1–11]. Then, on the base of the acquired knowledge, tailored preventive conservation strategies can be successfully selected and evaluated including climate control, environmental monitoring, selection of appropriate materials for manufacturing and assembling the display cases and for their design [1–6].

In order to reveal the presence of dangerous environmental species, in the present work Ag-based reference alloys with chemical composition and metallurgical features similar to those of ancient alloys were exposed to the open atmosphere and to a showcase of the Egyptian Museum (Cairo, Egypt). This latter museum is one of the most important of the Mediterranean basin hosting the most fascinating and grandiose collection of Egyptian art in the world constituted by more than 150,000 pieces.

The Ag-based alloys were purposely produced and exposed to have suitable materials to be sacrificed in order to understand

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what really happens at a micro- and nano-scale on the surface of silver objects exposed in that rooms or showcases instead of sampling precious archaeological artefacts or to evaluate environmental parameters such as temperature, humidity and gas concentration.

The micro- and nano-chemistry and morphology of the exposed alloys has been investigated by using a multidisciplinary analytical approach based on surface sensitive techniques such as micro-Raman spectroscopy (μ -Raman), selected area X-ray photoelectron spectroscopy (SA-XPS), X-ray diffraction (XRD), optical microscopy (OM) and scanning electron microscopy + energy dispersive spectrometry (SEM + EDS).

2. Experimental

2.1. Ag-based alloys production

The indoor atmospheric corrosion tests were performed on two typologies of Ag-based alloys with the following chemical composition expressed as weight percent (wt%): Ag 97.0, Pb 1.5, Cu 1.5 (alloy CNR91) and Ag 92.5, Cu 7.3, Pb 0.2 (alloy CNR141). The chemical compositions have been selected being commonly used for minting of coins and for manufacturing precious artefacts from the Phoenician Punic ages to the Roman period [1,14,19].

It is worth noting that we have produced the Ag-based alloys because the commercially available modern Cu or Ag-based alloys could be characterised by chemical compositions and metallurgical features different with respect to the ancient ones [19–25]. Even the use of pure metal substrates (Ag, Cu), generally diffused in the literature for testing innovative materials for conservation and to simulate archaeological corrosion phenomena, could be not appropriate when ancient alloys are considered because of the different degradation behaviour.

The Ag-based alloys have been produced by using pure granulated Ag, Cu and Pb metals that have been melted in a purposely designed graphite crucible placed in an electrically heated furnace and rapidly cooled down at room temperature (r.t.). A reducing atmosphere was used to limit the variation of the chemical composition and the porosity in the cast material [19,26,27] because during melting or casting of silver alloys, in presence of a slight oxidising environment, selective oxidation phenomena may take place. Furthermore, oxygen may be dissolved in the liquid alloy and successively released during solidification [19,26,27] and Cu_2O may be formed due to the reaction of copper with oxygen. Because of its higher reactivity with respect to silver, copper behaves like a deoxidiser and forms a copper-cuprous oxide eutectic with 3.5% Cu_2O (melting point = 1066 °C) localised at the grain boundaries of the solidifying metal.

In order to account for the heterogeneous metallurgical features of the archaeological alloys, a set of the Ag-based alloys in as cast conditions (referred in the text as AC) have been used to produce suitable disks for the experimental activities and another set have been thermally treated at 300 °C for 20 min in a tubular furnace under an inert atmosphere, hot mechanical worked to simulate the shaping or the coinage processes that induce elongation and metallurgical variations and then annealed at 400 °C under a CO reducing atmosphere for 10 min (referred in the text as TTMC) [14,19].

The as cast ingots (AC alloys) and the mechanically worked ingots (TTMC alloys) have been shaped to produce disks with a diameter of 15–18 mm and a thickness of 2 mm. The disks have been polished by using carborundum papers and diamond pastes up to 1/4 μm in order to obtain a flat and smooth surface with a mirror-like finish. After polishing, the Ag-based alloys have been cleaned with ethanol in an ultrasonic bath in order to remove oil, grease, dirt or other contaminating compounds and then dried and stored under a dry nitrogen atmosphere.

2.2. Exposure at the Egyptian Museum (Cairo, Egypt)

The samples of the Ag-based alloys have been subjected to a long-term indoor exposure in the Egyptian Museum of Cairo (Egypt) for 6 months in two different locations:

- first floor: to the atmosphere of a showcase (room 37) where are exposed precious silver and gold based artefacts of the Queen Hetepheres mother of the Pharaoh Cheope including some silver bracelets found in the Giza area and decorated with coloured enamels;
- second floor: to the open atmosphere of a corridor on a shelf about 3 m above the ground.

The locations have been chosen in order to evidence the difference between the atmospheric environments and the long-term exposure has been selected because shorter times could be not sufficient to produce silver sulphate/sulphite corrosion products [28–30].

2.3. Micro-chemical, morphological and structural analysis by SEM-EDS, OM and XRD

Micro-chemical and -morphological characterisations were performed by means of a scanning electron microscope (SEM) Cambridge 360 equipped with a LaB_6 filament and a high brilliance LEO 1530 field emission scanning electron microscope (FE-SEM) apparatus equipped with an energy dispersive X-ray spectrometer (EDS) INCA 250 and INCA 450, respectively, and a four sectors back-scattered electron detector (BSE) [31,32].

Optical microscopy (OM) investigations were performed by using a Leica MZFLIII microscope equipped with a digital camera (Leica DFC 320).

The micro-structural identification of the crystalline phases formed on the exposed Ag-based alloy disks was determined by a Siemens 5000 X-ray powder diffractometer using a Ni-filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Angular values in the range 10–80° in additive mode, a step size of 0.05° and a sampling time of 2 s were the experimental parameters used for data acquisition. In order to identify the crystalline species X-ray diffraction patterns analysis was carried out by using electronic databases.

2.4. X-ray photoelectron spectroscopy analysis

The surface chemical composition has been investigated by using an ESCALAB MkII (UK) (VG Scientific) spectrometer, equipped with a standard Al $\text{K}\alpha$ excitation source and a five-channeltron detection system. More experimental details on XPS technique have been reported elsewhere [14,18,33]. Some XPS spectra have been acquired also by using a monochromatized spectrometer Escalab 250Xi (Thermo Fisher Scientific, UK) equipped with six-channeltron detection system for spectroscopy and with an electron flood gun for charge neutralisation. In the analysis chamber, the surface of the samples was sputtered by using an EX-06 Ar^+ ion gun at 2.0 keV energy. Spectroscopic data were processed by the Advantage v.5 software.

In order to reduce the sample damage introduced during XPS measurements via dehydration, X-ray induced reduction and decomposition, short acquiring times have been used as well as a special suited copper sample holder cooled by means of liquid nitrogen [34].

2.5. Micro-Raman analysis

Micro-Raman (μ -Raman) analysis was performed at room temperature using a Renishaw 2000 μ -Raman instrument equipped

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