



Full Length Article

X-ray Photoelectron Spectroscopy as a tool to investigate silane-based coatings for the protection of outdoor bronze: The role of alloying elements



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ABSTRACT

Application of a protective coating is the most widely used conservation treatment for outdoor bronzes (cast Cu-Sn-Zn-Pb-Sb alloys). However, improving coating protectiveness requires detailed knowledge of the coating/substrate chemical bonding. This is particularly the case for 3-mercaptopropyl-trimethoxy-silane (PropS-SH) applied on bronze, exhibiting a good protective behaviour in outdoor simulated conditions. The present work deals with X-Ray Photoelectron Spectroscopy (XPS) and Electron Microscopy (FEG-SEM + FIB (Focused Ion Beam)) characterization of a thin PropS-SH film on bronze. In particular, in order to better understand the influence of alloying elements on coating performance, PropS-SH was studied first on pure Cu and Sn substrates then on bronzes with increasing alloy additions: Cu₈Sn as well as a quinary Cu-Sn-Zn-Pb-Sb bronze. Moreover, considering the real application of this coating on historical bronze substrates, previously artificially aged ("patinated") bronze samples were prepared and a comparison between bare and "patinated" quinary bronzes was performed. In the case of coated quinary bronze, the free surface of samples was analysed by High Resolution Photoelectron Spectroscopy using Synchrotron Radiation (HR-SRPES) at ANTARES (Synchrotron SOLEIL), which offers a higher energy and lateral resolution. By compiling complementary spectroscopic and imaging information, a deeper insight into the interactions between the protective coating and the bronze substrate was achieved.

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1. Introduction

Cultural Heritage in outdoor conditions naturally undergoes a degradation process that can severely damage the historical

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and cultural traces of this heritage. This is typically the case for outdoor bronzes, which suffer corrosion inducing specific patinas on metallic surfaces [1,2]. Particularly in urban atmosphere, corrosion phenomena lead to a marked degradation of bronze monuments, making patinas partially leachable, as demonstrated by green streaks on stone basements. In this context, the application of protective coatings remains the best solution for limiting corrosion damage of outdoor bronzes, as suggested in the last decades [3].

As regards protective treatments, organosilane coatings attracted a significant research attention in recent years, due to their protective efficiency towards the corrosion of several alloys in outdoor conditions. Research studies on the protection of copper

and copper-based alloys were mainly carried out on octadecyltrimethoxy-silane [4], glycidioxy-propyl-trimethoxy-silane [5] and γ -aminopropyltriethoxysilane (γ -APS) [6]. However, outstanding results were obtained with silanes containing sulphur or mercapto-groups, such as 3-mercapto-propyl-trimethoxy-silane (PropS-SH) [6–14].

The protective properties of PropS-SH coatings are connected to the formation of silanol groups (Si–OH) during silane hydrolysis and to their subsequent condensation in a polymeric dense Si–O–Si network [8].

On copper and copper alloys, surface chemisorption of PropS-SH through metal thiolate (Me–S–C) [7] and metal siloxane (Me–O–Si) bonds [15] ensures the desirable adhesion to the metal substrate.

In general, in the Cultural Heritage field the selection of protective coatings and corrosion inhibitors therein requires taking into account the following key points: (i) a basic understanding of the corrosion mechanism and (ii) testing the efficiency and the aesthetical impact of the candidate treatments on representative substrates, which reproduce in a reliable way the complexity of real surfaces. Therefore, in the present work, a quinary bronze was prepared with the typical microstructure and morphology of cast bronzes. Subsequently, investigation was performed with the aim to reproduce the typical corrosion features of unsheltered areas in real outdoor bronze monuments and to investigate the chemical bonding between coating and aged substrate (key point (ii)). Bronze samples were exposed to conditions closely simulating outdoor exposures [16,17] and in particular to runoff conditions (through dropping test). The tested protective coating was obtained from PropS-SH, selected on the basis of previous electrochemical tests and accelerated ageing tests performed on the same bronze alloy [11,13].

In order to achieve a better comprehension of the chemical bonds between Cu-based alloys and PropS-SH, Cu-based substrates with different alloying elements and pure tin were selected for the application and study of PropS-SH coating. Specifically, beside tin, investigations were performed on pure copper, binary tin-bronze alloy (Cu8Sn) and the more complex quinary alloy, also aged under conditions similar to those induced by outdoor dropping rains. XPS spectroscopy is one of the most appropriate techniques to characterize coatings and their interaction with substrates. In particular, in this study concerning the coated bare quinary bronze, High Resolution Photoelectron Spectroscopy using Synchrotron Radiation (HR-SRPES) at ANTARES (Synchrotron SOLEIL) has been applied for the first time offering higher energies and lateral resolution [18].

2. Materials and methods

2.1. Materials

Quinary bronze was used as the main substrate for coating application. The composition of quinary bronze is: 91.9 Cu, 2.4 Sn, 1.0 Pb, 2.9 Zn and 0.8 Sb (wt%). It has a typical dendritic as-cast microstructure with cored α -solid solution (i.e. local enrichment of Sn and Sb elements in the interdendritic spaces) also including non-miscible lead globules as detailed in [12,14]. Shrinkage due to cooling during the casting process was also observed, inducing the formation of micro-cavities.

Pure copper (Cu) and tin (Sn) metals (purity higher than 99.99 wt%), as well as a binary bronze alloy with 8 wt% Sn (Cu8Sn) were used as reference materials. Moreover, in order to investigate coating properties in the absence of interactions with bronze elements, also a non-metallic, ceramic substrate (zirconium nitride, ZrN) was prepared.

Only in the case of quinary bronze, both bare and patinated conditions were considered. The patination simulating natural patinas was performed by accelerated ageing test using a Dropping test device, described in detail elsewhere [17]. A synthetic rain solution (pH = 4.3) was periodically dropped onto 45° inclined specimens through four rain channels per specimen, in order to maximize the aged surface, with alternated cycles of 2-days dropping/1-day drying, 3-days dropping/1-day drying. The Total Time of Wetness (ToW) was 30 days. The acid rain solution was prepared on the basis of ambient samples collected at a monitoring station in Bologna, Italy, with composition reported in [19]. The dropping tests simulate the runoff condition of outdoor bronzes due to unsheltered exposure to rainwater. The application of this accelerated ageing test was previously found to produce representative patinated substrates, comparable to natural patinas, suitable for testing protective treatments [20].

Artificially patinated quinary bronze was characterised by a rough surface, with a corrosion-modified layer of variable thickness, higher within the core of the dendrites than in the peripheral areas, due to preferential dissolution of copper and zinc from the alloy [12,14,17].

2.2. Preparation and characterisation of PropS-SH coating

Before coating application, the surfaces of bare samples were prepared by emery papers, then polished by using diamond spray with decreasing particle size (down to 1 μ m), washed with deionized water and degreased with acetone. Instead, the rough artificially patinated surface (quinary bronze) was silane coated without any surface preparation.

In order to prepare thin coatings suitable for XPS analysis of coating/metal interfaces, bare samples of Cu, Sn, Cu8Sn and quinary bronze were immersed (“dip-coated”) for short times (150 s) in hydrolysed silane solution (90/5/5 v/v ethanol/water/PropS-SH) at pH = 4, followed by fast withdrawal (Table 1). Then, the samples were washed by ethanol to eliminate physisorbed silane molecules. The obtained coatings were few nanometers thick as evaluated by weight gain measurements, assuming a density value of 1.1 g cm⁻³ for PropS-SH. By prolonging to 1 h the immersion time in hydrolysed silane solution, thicker coatings on ZrN were prepared, which permitted to investigate the coating bulk on a corrosion resistant substrate by XPS (Table 1).

1 h dip coating is often adopted for PropS-SH to protect efficiently bronzes from corrosion [11–14]. Therefore on patinated quinary bronze, these thicker coatings were also applied to analyse their cross section stratigraphy and for surface XPS and HR-SRPES investigations.

All the coated samples were cured at room temperature for at least 10 days before analyses. Finally, uncoated bare quinary bronze were used as representative substrate for XPS measurements in order to check the initial state of bronze surface before coating application. The surface was analysed after the polishing previously described.

XPS analysis, performed on the samples collected in Table 1, was carried out by using a monochromatised Al K α ($h\nu = 1486.7$ eV) source on a ThermoScientific K-Alpha system. The X-ray spot size was about 400 μ m. The pass energy was fixed at 130 eV with a step of 1 eV for surveys and 40 eV with a step of 0.1 eV for core levels. Ionic Ar⁺ sputtering of the surfaces was not applied in order to avoid modifications of the organosilane. The analysed core levels (C 1s, O 1s, Si 2p, S 2p, Cu 2p, Zn 2p, Sn 3d, Pb 4f) were calibrated against C 1s binding energy (conventionally BE = 284.6 \pm 0.1 eV). XPS data were fitted by using Thermo Scientific™ Avantage Software and the background signal was removed by using Shirley method. Flood gun was also applied for avoiding charge effects.

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