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Corrosion assessment of a bronze equestrian statue exposed to urban environment / Es Sebar, L.; Iannucci, L.; Grassini, S.; Angelini, E.; Parvis, M.; Antonino, R.; Quaranta, G.; Giani, C.; Boassa, M.; Nicola, M.. - In: KOROZE A OCHRANA MATERIALU. - ISSN 1804-1213. - ELETTRONICO. - 66:1(2022), pp. 50-55. [10.2478/kom-2022-0008]

Publisher:
Sciendo

Published
DOI:10.2478/kom-2022-0008

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This paper presents the characterization of the conservation state of a bronze equestrian statue exposed outdoor, through an in-situ, multi-analytical, and non-invasive approach. The artefact under study is a bronze equestrian statue, devoted to Alfonso La Marmora, placed in an urban environment in the city of Turin. The investigation was carried out in the framework of a restoration intervention, with the principal aim of characterizing the overall conservation state of the sculpture to provide the conservators with information useful to develop a tailored restoration plan. X-ray fluorescence spectroscopy (XRF) was carried out for the identification of the elements present in the artefact alloy, showing that the statue was made using mainly two bronze alloys. Electrochemical Impedance Spectroscopy (EIS) was performed to study the corrosion mechanisms and to define the protective effectiveness of the patina present on the surfaces. Eventually, Raman spectroscopy (RS) was performed to characterize the chemistry and microstructure of the corrosion products, mainly identified as sulphates. The combination of these techniques allowed to confirm the presence of wax layers from previous restoration work, still capable to protect the metal substrate against corrosion. In addition, it was possible to correlate the conservation state to the exposure conditions and location on the statue.

INTRODUCTION

Preservation of cultural heritage metallic artefacts exposed outdoors is an issue of paramount importance, sometimes underestimated in its complexity and not properly addressed. In this corrosion field, urban environments represent a particularly severe case study because the weathering effect is worsened by pollution and by the presence of aggressive compounds in the atmosphere [1-3]. For all these reasons, great attention should be paid to the characterization of the degradation mechanisms affecting metallic cultural heritage, also assessing the corrosion protection effectiveness of restoration interventions performed during the years. Moreover, as the investigated objects are artefacts of great historical and artistical value, the use of non-invasive techniques is generally mandatory, in order to avoid any loss or modification of the object [4].

Patina formation on bronze artefacts is influenced by multiple factors, such as pollutants concentration in air (e.g. sulphur dioxide) [5-7], environmental parameters such as temperature and relative humidity [8], and also orientation in space of the surface. Actually, many studies have demonstrated that rain washout and water evaporation rate on different surfaces leads to the formation of different copper corrosion products [9,10]. Moreover, artefacts exposed outdoor are generally coated using protective organic varnishes or waxes, which have a strong influence on the subsequent electrochemical behaviour of the material [11,12]. In particular, during the years these organic superficial layers should be characterized in order to assess their long-term protection effectiveness.

The work presented in this paper deals with the characterization of the conservation state of an equestrian statue devoted to General Alfonso Ferrero della Marmora. The monument is located in a central square of Turin (Italy) and it was built up in 1891, thirteen years after the decease of the General. The monument was designed by Stanislao Grimaldi and the bronze statue was cast in Turin in the Regio Arsenale (Royal Arsenal).

DOI: 10.2478/kom-2022-0008

In 2006 a complete restoration of the monument has been performed, as multiple ongoing degradation phenomena required an urgent intervention [13]. During the intervention, the presence of different copper sulphates, namely brochantite, chalcanthite, and antlerite, was underlined, together with some organic deposits probably related to smog and pollution. The black patinas were mechanically removed and a new protective system composed of corrosion inhibitors and wax was applied.

In 2020, more than ten years later, a new restoration intervention has been carried out, together with a new campaign of analytical measurements. The main goal of this study was the assessment of the conservation state of the bronze elements, the documentation of the new corrosion products layers grown on the metallic surface and the identification of the ongoing corrosion processes that could compromise the integrity of the artwork. Specifically, the survey was performed in order to collect data to support restorers in the definition of specific conservation practices, based on the nature of the corrosion patinas and their electrochemical stability. An in-situ multi-analytical approach was employed, so that both the protective effectiveness and the chemical-physical properties of the superficial layers could be analysed.

Fig. 1. Picture showing the equestrian monument devoted to Alfonso Ferrero della Marmora

EXPERIMENTAL

The monument devoted to Alfonso Ferrero della Marmora

The equestrian monument, shown in Figure 1 in a picture taken after the restoration performed in 2020, is located in the centre of Piazza Bodoni in Turin (Italy). The monument is composed of a bronze equestrian statue depicting General Alfonso Ferrero della Marmora (also named Alfonso La Marmora), placed on a pink-granite base. At the four corners of the base there are four bronze lion heads; on the base there are also other decorative elements in bronze such as the coats of arms of the Ferrero della Marmora family and of the city of Turin and several inscriptions.

The analytical approach

The overall conservation state of the monument was assessed by means of in-situ multi-analytical and non-invasive methods. The study aimed to identify and characterize the corrosion products present on the artefact and the ongoing degradation mechanisms, by means of portable, non-invasive and non-destructive techniques. As initial survey, X-ray fluorescence spectroscopy (XRF) was performed in multiple areas of the artefact in order to assess if different alloys were used for the realization of the statue. Then, discriminating on the basis of their visual appearance and colour, different patinas were analyzed by means of Electrochemical Impedance Spectroscopy (EIS), in order to evaluate their electrochemical stability. Finally, the patinas were analysed by means of Raman Spectroscopy (RS), to identify the different corrosion products and thus relate the different electrochemical stability with the chemical-physical nature of the surface layers.

X-ray Fluorescence Spectroscopy

The elemental composition of the alloys constituting the statue was investigated by means of XRF. The used instrument is a Bruker Tracer 5i analyser (Rhodium excitation source), which is portable and allows to perform non-invasive analyses. The analyses were performed setting the voltage to 40 kV and the current to 40 uA, with an acquisition time of 30 s and a collimator of 3 mm. Collected spectra were processed using the Artax Spectra (8.0.0.476) software to perform the Bayesian deconvolution of the collected spectra and to remove any elemental interference and background signal. Data were then processed by means of principal component analysis (PCA) in order to identify possible similarities among acquired spectra. A Python script based on the Scikit-learn library was used, processing the acquired spectra as input data for the analysis [14,15].

Electrochemical Impedance Spectroscopy

EIS was employed to study the corrosion mechanisms and to assess the protective effectiveness of the different patinas present on the monument. Also for this technique a portable instrument was used, namely the Ivium-CompactStat.e 10800. A 3D-printed electrochemical cell, specifically designed by Politecnico di Torino for performing impedance measurements in totally non-invasive way without affecting the corrosion patinas, was fixed on the metal surface and easily removed after the measurement. The cell has a two-electrode configuration: the bronze statue is connected to the working electrode, and a platinum wire is employed as counter electrode [16,17]. A 0.1 M sodium sulphate (Na_2SO_4) solution was used as the electrolyte; the analysed area was equal to about 0.78 cm^2. EIS measurements were performed by applying an alternating voltage of 20 mV, while compensating the open corrosion potential (E_{OCP}), in the frequency range from 0.1 Hz to 100 kHz.

Raman Spectroscopy

In order to identify the chemical features of the corrosion patinas present on the bronze sculpture, RS measurements were used. The analyses were carried out using a portable instrument, i.e. the i-Raman Plus (BWTEK), provided of a green excitation laser (532 nm), and a spectrometer (BWS465-532S) that works in the range from 150 cm^{-1} to 4200 cm^{-1} (resolution of 7.3 cm^{-1}). The analytical conditions were chosen to avoid any modification of the investigated material [18]: laser power of 6 mW, integration time of 30 s and 3 repetitions on each area of analysis. Spectrum baseline was computed using the 'Vancouver Raman Algorithm', as described in [19].

RESULTS AND DISCUSSION

At visual inspection, the monument was characterized by the presence of patinas having different colours and aesthetical appearance, presumably corresponding to different conservation states. Colours ranged from light to dark green and some areas were covered by a blackish patina, presumably due to smog and particulate deposits. The initial survey was performed using XRF, in order to understand if the statue had been made from a single material or if different copper-based alloys were present. In some of the points, chosen considering the patina visual appearance, EIS and RS measurements were performed too, in order to have a complete characterization of the superficial layers. About 180 areas were analysed by means of XRF, and about 20 of them were also analysed using EIS and RS; the most significant ones are reported in Figure 2.

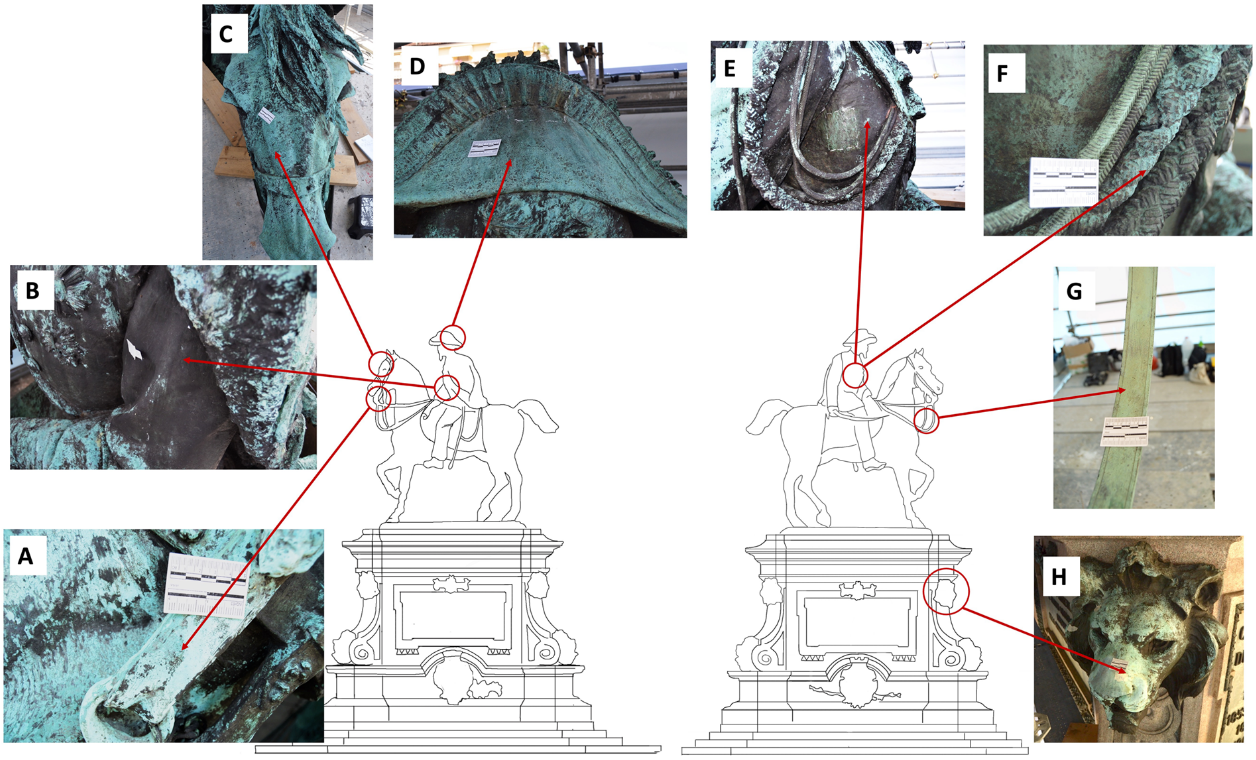


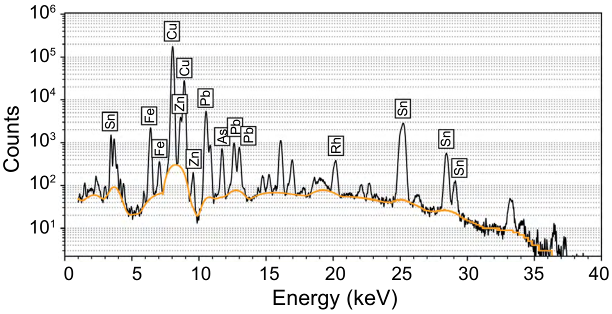
Fig. 2. Photographs of the most significant analysed areas, representative of the different colours and morphologies of the corrosion products, and their position on the statue

Results from XRF measurements showed that there are two main alloys used for the realization of the monument. The first one, whose characteristic XRF spectrum is reported in Figure 3a, was employed for the main body of the statue, namely for the horse and for the knight body (areas A, B, C, D, E, and H in Figure 2). The alloy is characterized by the presence of copper, tin, zinc, iron, lead, and arsenic, which are common elements in bronzes composition for artistic foundry; meanwhile rhodium characteristic lines at 20.22 keV are related to the anode material of the spectrometer. This finding is in agreement with the analyses performed during the previous restoration intervention which identified a ternary bronze constituted by copper, tin and zinc (90 wt%, 6 wt% and 4 wt%, respectively). In the 2006 campaign, the bronze composition was identified by means of EDS (Energy Dispersive X-ray Spectrometry) after a microsampling of the material. On the contrary, the experimental approach presented in this paper and based on XRF in-situ measurements, allowed analysing many different areas of the statue, thus highlighting the homogeneity in the alloy composition. As a matter of facts, the obtained results confirmed that the entire knight statue was made of the same bronze alloy. Moreover, it is important to underline that the discrepancies between these new data and the previous ones can be attributed to the fact that the EDS sampling was necessarily performed by taking the material from edges and undercut, where local inhomogeneities in the alloy composition could be present.

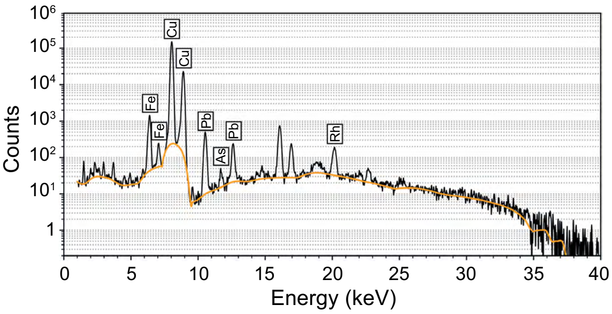
A second alloy was then identified in the decorative parts of the monument, namely the horse bridles and the decorations on the La Marmora blouse (areas F and G in Figure 2). Also this alloy is a bronze, characterized by the presence of copper, iron, lead and arsenic, as can be seen from the XRF spectrum reported in Figure 3b. PCA was also used in order to check if additional alloys could be discriminated among the acquired spectra, but only the two reported groups were identified.

After performing the compositional analysis, EIS was used in order to assess the protective effectiveness of the various corrosion products layers and of the organic protective layers applied during the previous restoration campaigns.

Two main cases were identified, based on the different trends in the impedance spectrum. The first one, reported in Figure 4 (area B in Figure 2), regards the areas with values of the impedance module above

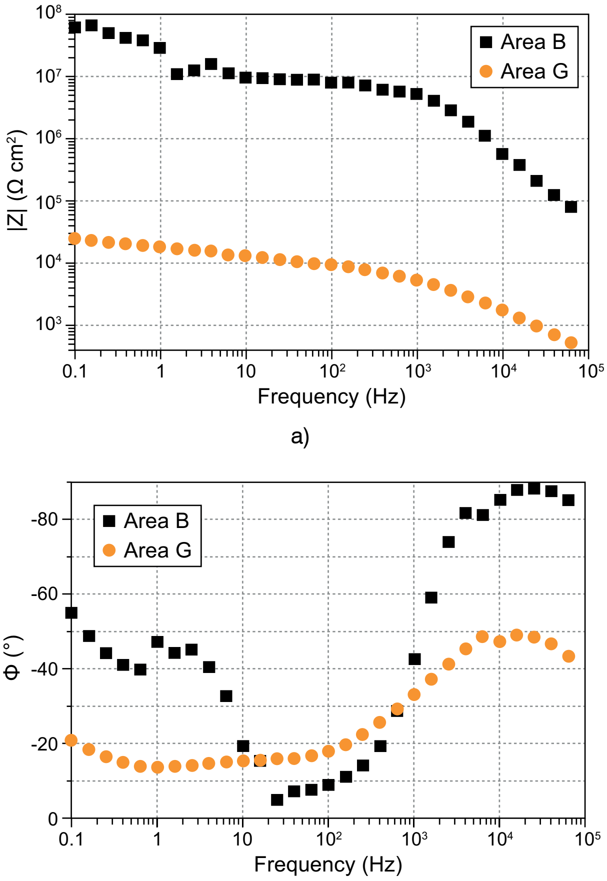


a) main body



b) decorative parts

Fig. 3. XRF spectra of the two alloys constituting the equestrian statue: a) main body (i.e. area C in Figure 2), b) decorative parts (i.e. area G in Figure 2) – in yellow the spectrum baseline



b)

Fig. 4. Impedance spectra acquired in different areas of the statue: area B – dark brown patina; area G – bright green patina (as shown in Figure 2)

10^6 Ω·cm² at low frequencies and phase values of about -90° at high frequencies. These areas are characterized by a good protective effectiveness of the surface layers and thus by a low corrosion rate for the metal substrate (areas B and E in Figure 2). The second case, reported in Figure 4 (area G in Figure 2), is related to the areas with lower impedance module values (about 10^4 Ω·cm²) at low frequencies and phase values which remained below -50° in the whole analysed frequency range and reached a value of about -10° at low frequencies. So, these points are characterized by a higher corrosion rate (as can be deduced from the absolute impedance value) and are presumably no longer protected by any organic layer applied during the previous restorations (areas A, C, D, G, and H in Figure 2).

It is worth to notice that it was possible to correlate the impedance spectra collected in the different areas of the statue with the colour of the patina and its exposure to the environment. Actually, areas with a high impedance module had a blackish or dark brown appearance, while those with a low impedance module had a bright green appearance. Moreover, in virtually all cases, areas characterized by high impedance module were vertically oriented or in sheltered positions. On the other hand, patinas with bright green appearance were found in areas more exposed to rain washout, such as the bicorn, the horse head and the bridles. So, the formulated hypothesis was that in areas exposed to intense rain the protective layers had been washed out during the years, exposing the bronze corrosion products to the environment (this explains the lower impedance modulus). Instead, sheltered or vertically oriented areas, preserved the applied protective layers, keeping a lower corrosion rate. Actually, impedance moduli in the range of 10^6 Ω·cm² or above are characteristic of organic coatings with high protective capability, while these values are too high to be attributed to a corrosion products layer naturally grown on the bronze surface.

In order to validate this hypothesis, RS measurements were carried out in most of the areas that were previously analysed by means of EIS. The results showed that wax residues were present in areas characterized by high impedance moduli. Actually, as can be seen from Figure 5, the Raman spectrum is composed by an intense fluorescence signal and two peaks, namely at 2843 cm^{-1} and 2876 cm^{-1}, characteristic of aliphatic chains and thus of organic material such as wax.

In areas with low impedance values at low frequencies, i.e. with low protective capability and bright green colour, the collected Raman spectra showed the characteristic peaks of sulphate-based corrosion products and the absence of peaks related to wax. As an example, in Figure 6 one of these spectra is shown, where the peaks at 410 cm^{-1}, 485 cm^{-1}, and 980 cm^{-1}, generally attributed to brochantite, are present [20,21]. The presence of this compound in the bronze patina is characteristic of copper alloys exposed to atmosphere in non-aggressive conditions and confirms the stable behaviour of the material as far as the corrosion processes are concerned [22].

The performed measuring campaign allowed the restorers to assess the quality of the intervention carried out about a decade before. Actually, even though rain washout removed part of the applied organic protective layers, critical situations could not be found, and the corrosion phenomena were under control in all areas of the monument. Chlorides-containing compounds could not be found in any of the analysed corrosion patina, further highlighting the good conservation state of the artefact. Based on these conclusions, only a soft intervention was necessary for the monument. Restorers performed a light cleaning of the entire surface of the statue by means of organic solvents to remove wax layers and then applied the new protective coating based on acrylic varnishes and microcrystalline wax.

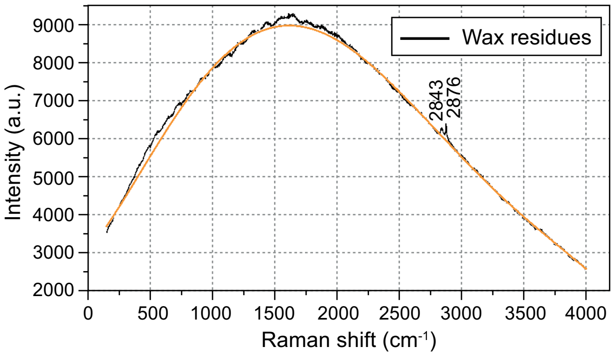


Fig. 5. Raman spectrum acquired in one of the 'blackish' areas in the statue (area E in Figure 2) – in black the acquired spectrum, in yellow the baseline (peaks, at 2843 cm^{-1} and 2876 cm^{-1} are characteristic of aliphatic chains)

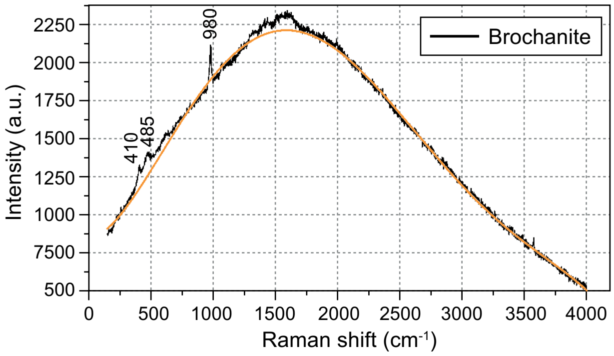


Fig. 6. Raman spectrum, identified as brochantite (characteristic peaks at 410 cm^{-1}, 485 cm^{-1}, and 980 cm^{-1}), acquired in correspondence to the 'bright green' areas in the statue (area G in Figure 2) – in black the acquired spectrum, in yellow the baseline)

CONCLUSIONS

This study showed the application of a multi-analytical and non-invasive approach for the characterization of the conservation state of a bronze monument. Thanks to the combination of the results coming from different diagnostic techniques, it was possible to fully characterize the materials constituting the artwork and to assess the protective effectiveness of the restoration intervention carried out about a decade ago. XRF measurements highlighted the presence of two different bronze alloys used to produce the statue. It is worth to note that these two alloys were characterized by similar corrosion processes, so alloy composition was not a discriminant for the degradation kinetics. On the other hand, the influence of surface orientation in space had a determinant influence on rain washout and thus on the stability of protective superficial layers applied during the previous restauration. Areas characterized by intense rain washout exhibited lower impedance values, as the wax layers had been progressively removed. In these areas of the statue, brochantite was the main corrosion product constituting the patina. Conversely, sheltered areas were characterized by high impedance values, typical of a protective superficial layer still present.

These results also highlight the importance to perform a regular assessment of the conservation state of metallic artefacts exposed to urban environments, in order to keep degradation processes under control, to avoid any significant deterioration and to develop tailored restoration interventions.

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