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A long-term corrosion investigation of bronze sculptures exposed outdoor

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Abstract – **Safeguarding our cultural heritage for the future generations is possible only by applying tailored conservation strategies. The safeguard is a complex task and often requires measurements to be performed on the artefacts. This paper describes an interesting case regarding the metallic artefacts belonging to the Gori Art Collection at Fattoria Celle (Pistoia, Italy). This collection of modern art, developed inside a project of environmental art, is facing different corrosion phenomena due to its permanent exposure to outdoor environmental conditions. A non-invasive and in-situ multi-analytical approach was recently started in order to assess the conservation state of the metal artefacts and to assure their long-lasting preservation trough the development of a conservation project. In this paper, the preliminary results of the monitoring campaign carried on the bronze sculpture "Cavaliere" by Marino Marini will be presented and discussed.**

I. INTRODUCTION

All artefacts belonging to our cultural heritage are facing ageing and conservative issues and therefore it is important to monitor carefully their conditions to assure their preservation over the time.

Moreover, heritage metal artefacts are critical as they have to face different corrosion phenomena due to their interaction with the environment. Identifying these mechanisms is possible only through a complete characterization of the corrosion profiles and products [4, 5, 6, 7]. This requires measurements, conducted preferably with a non-invasive approach to avoid damaging the artefacts themselves. In addition, to have a deep understanding of the reasons that lead to the corrosion of the artefacts, it is often important also to investigate the environmental conditions in which the artefacts are stored, displayed or installed. Indeed, relating the corrosion processes with the environment allows one to define which are the parameters which mostly affect the corrosion reactions occurring on the objects and the stability of the corrosion products layers formed on the metallic surface.

Of course every installation has different requirements in terms of measurements and monitoring issues so that a universal solution cannot be given. However often the basic requirements are the same so this paper discusses a monitoring campaign that was carried out on the metallic artefacts belonging to the Gori Art Collection, situated in Fattoria Celle, in Pistoia (Italy) [8]. This project represents an interesting example whose conclusions can be easily extended to many other cases.

The collection was formed over two periods: the first one from 1950 to 1970 in Prato (Italy), while the second one started in 1970 in Fattoria Celle. The collection was due to the desire of Pina and Giuliano Gori who required various artists to create works of contemporary art, within a project of environmental art. The idea was to connect sculptures and installations with the surrounding spaces, making them an integral part of the artworks.

Many sculptures and installations within this private collection, are installed outdoor, in the gardens, with no protection from the atmospheric conditions thus being examples of the atmospheric corrosion phenomena affecting metals. A monitoring campaign was carried out with the goal of designing conservation strategies and procedures for the protection of these artefacts.

In particular, in this paper the case study regarding the sculpture "Cavaliere" by the Italian artist Marino Marini is presented. The "Cavaliere" is a bronze sculpture, realized in the 1980 and installed in the private garden of the Villa. Notwithstanding, the recent realization of this sculpture, the existing information regarding its realization and the material employed is quite limited. In addition, the area in which the artefact is placed is surrounded by trees and exposed to sun and rain, in touch with the soil and with no protection and the artefact cannot be moved.

An in-situ multi-analytical approach was the most suitable solution in order to reach the main goal of this project for this situation. Corrosion phenomena were investigated by means of electrochemical impedance spectroscopy

Fig. 1. The sculpture "Cavaliere" by Marino Marini

(EIS), while chemical and microstructural characterization of the corrosion patinas were performed through portable Raman spectroscopy and X-ray diffraction (XRD). Eventually, a 3D photogrammetry survey was performed to collect a complete artefact documentation.

The monitoring campaign started in 2018 and it is still in progress. This kind of characterization is necessary in order to develop conservation projects regarding for example cleaning and restoration procedures or the application of specific coating for the protection towards corrosion phenomena [9]. Furthermore, the monitoring campaign could be integrated with a remote accessible solution as the one presented in [10].

The preliminary results obtained till now are presented in this paper.

II. MULTI-ANALYTICAL APPROACH

A. *In-situ EIS measurements*

Electrochemical impedance spectroscopy is a valid technique for the assessment of the protective properties of the corrosion patinas, together with the stability of corrosion reactions occurring on the surface of an object.

In this case measurements were performed in situ, with a non-invasive approach. This allows one to relate the electrochemical behaviour of the investigated surface to the environment in which the artefact is regularly exposed. Therefore, it is possible to study the effect that atmospheric conditions have on the corrosion phenomena and products.

EIS measurements were performed by means of a portable commercial interface (Ivium-CompactStat.e 10800) coupled with measuring probes, specifically designed to be suitable for the analysis in cultural heritage field. The probes can be positioned on the investigated surface thanks to a polyurethane disk and to a double-side bonding tape, that leaves no traces when removed (Fig.2). The probes are two-electrodes cells, with a platinum wire as reference/counter, whereas the metal artefacts is the working electrode. The probes are realized in acrylonitrile butadiene styrene (ABS) by means of a 3D printer. They have a 30 mm diameter, 20 mm thickness and the measuring surface area has a diameter of 8mm [11].

All measurements were performed by stimulating the artefact with a small alternating voltage (range: 10-100 mV), while the open corrosion potential (EOCP) was measured and compensated. The electrolytic solution employed was Na_2SO_4 0.1 M and the EIS spectra were collected in the frequency range from 0.01 Hz to 100 kHz.

B. *XRD and Raman spectroscopy measurements*

A morphological and chemical characterization of the corrosion products was performed in order to correlate them to the corrosion reactions occurring on the surface.

Portable Raman spectroscopy was the technique employed in situ for the chemical and microstructural analysis of the corrosion patinas.

Raman measurements were performed by means of the i-Raman Plus portable apparatus with a green excitation laser (wavelength: 532 nm) and BWS465-532S spectrometer (range: 150 - 4200 cm-1, resolution 7.3 cm-1) coupled with a CCD sensor with high quantum efficiency and wide dynamic range assisted by a cooling system. The measurements were performed a value of the laser power equal to 6 mW, with an integration time of 30 s, performing 3 repetitions for each area.

For performing XRD few micrograms of samples were collected The sampled corrosion products were analysed by X-Ray diffraction (PAN analytical X'Pert PRO). XRD patterns were collected using a Ni-filtered $CuK\alpha$ radiation (Kα_1 [Å]:1.54060, Kα_2 [Å]:1.54443). The measurements were carried out setting generator current and voltage respectively to 40 mA, 40 kV, using a step size of 0.026° and a scan speed of 0.047746 °/s. The patterns were collected in the range between 10 and 90°. The crystalline phases identification was performed by using the HighScore Plus software.

C. *Photogrammetry 3D survey*

Photogrammetry measurements were used to perform a complete documentation of the sculpture conservation

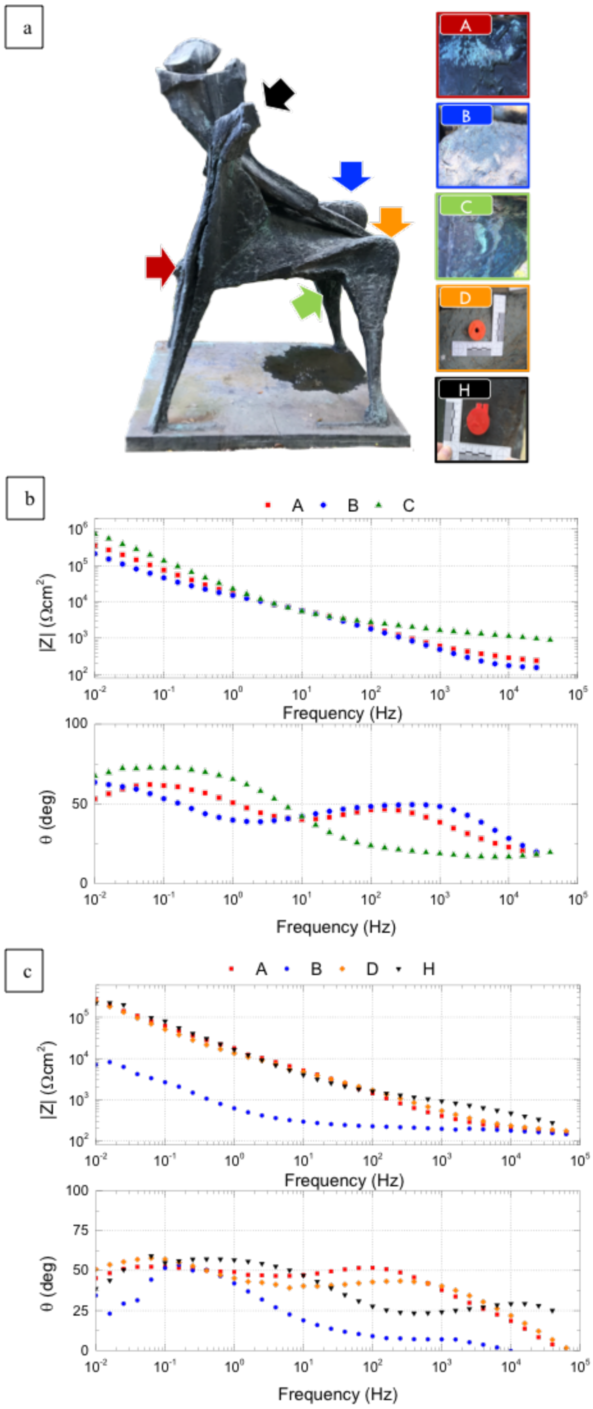

Fig. 2. a) Image of the sculpture and of the analysed areas; b) EIS spectra collected during the first campaign; c) EIS spectra collected during the second campaign

state. A Nikon D3100 with Nikkor lens 18-55 mm was used for image acquisition. The lens focal length was fixed at 18 mm, with an aperture of f/6.3 in order to have sharp images, an exposure time of 1/125 and a sensitivity of ISO 400. Markers were inserted within the acquisition scene to facilitate the alignment procedure. The marker distance was measured in order to scale the final model. Images were taken around the sculpture at different heights (3 rings) and even close-up images were acquired to define the complicated areas: Fig. 2b shows the acquisition strategy. Eventually, an image of a colour chart with the sculpture was acquired. The images were acquired and saved in RAW format. Agisoft Photoscan Professional (1.2.5) software was used for the 3D model construction.

III. RESULT AND DISCUSSION

A. *In-situ EIS measurements*

Fig. 2 shows as an example some impedance spectra, recorded on the bronze sculpture exposed to atmospheric corrosion. Electrochemical impedance measurements were carried out in different areas of the work's surface that presented different coloured patinas. Fig. 2a shows the impedance spectra recorded during the first measurement campaign carried out in November 2018 along with the images of the corresponding areas and their position. The impedance spectra allow one to distinguish between two different electrochemical behaviors. Spectra recorded on points A and B, characterized respectively by the presence of a black patina with bright green crystals and a light green one, present a similar impedance module and phase. On the contrary, point C, with a more homogeneous bright green patina, differs mainly in the phase trend. Spectra recorded at points A and B are characterized by an impedance magnitude value, | Z |, higher than $10^5 \Omega x cm^2$ at low frequencies, confirming the good electrochemical stability of the patina. The phase trend, higher than 50° at low frequencies, indicates a capacitive-diffusive behaviour correlated with the presence of a layer of corrosion products characterized by porosity. Point C instead presents an impedance spectrum with module values that approximate $10^6 \Omega x cm^2$, with a phase that approximates resistive values at mid and high frequencies. Overall, the impedance measurements show the good protective effectiveness of corrosion patinas.

Measurements were repeated six months later in order to assess stability and protective effectiveness of the patinas as a function of the exposure time to atmospheric corrosion. In addition to measurements on areas A and B, two new areas referred to as D and H, characterized respectively by a compact black patina and a light green one, similar to that of the area B, were carried out. Fig. 2c shows the Bode graphs recorded on the points analysed. Images and position of the analysed areas are shown in Fig. 2a.

As it can be observed, the A, D and H spectra show a similar behaviour of the impedance magnitude |Z|, with values at low frequencies above $10^5 \Omega x cm^2$. The capacitive trend of the phase approaches 45 ° at low frequencies, possible index of the presence of porosities in the corrosion products layers and diffusion phenomena. Spectrum

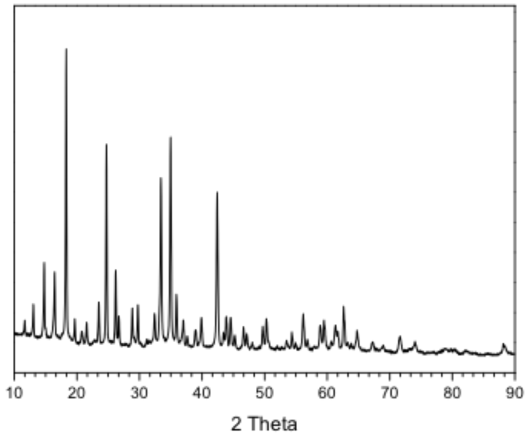

Fig. 3. XRD pattern collected on bright green sample

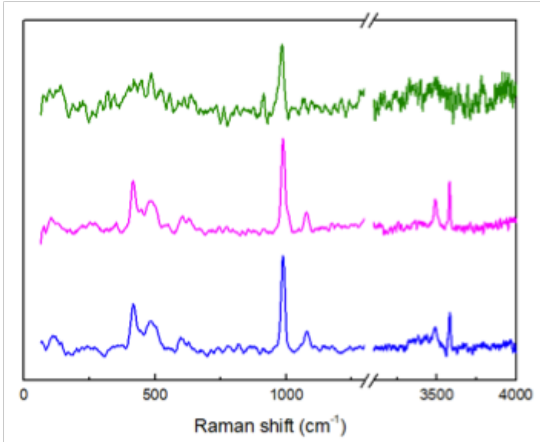

Fig. 4. Raman spectra collected on tree points on the sculpture

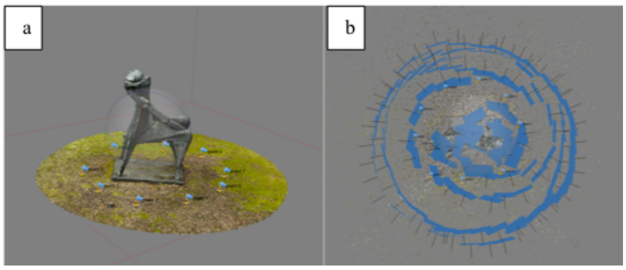

Fig. 5. a) Dense cloud with markers; b) acquisition strategy

at point B shows lower magnitude values of about one order of magnitude at low frequencies and a mostly resistive phase trend. Overall, the measurements suggest a good protective power of corrosion patinas.

Comparison of impedance magnitude and phase at points A and B allows one to underline the importance of repeated impedance measurements over time. In fact, comparing spectra at a distance of six months, it is possible to notice that the patina present at the A area maintains a good protective capacity as highlighted by the impedance module at low frequencies, which remains higher than $10^5 \Omega x cm^2$. On the contrary, in area B the impedance magnitude after 6 months is significantly lower (about one order of magnitude), showing an increase in degradation phenomena and a lower barrier capacity of corrosion product layer.

B. XRD and Raman spectroscopy measurements

The micro-samples were investigated through XRD analysis. The collected patterns (an example is reported in Fig. 3) allow one to identify manly the presence of Antlerite.

The recent acquisition of a portable Raman instrumentation allowed us to perform an in-situ chemical identification of the patinas in different points of the sculpture.

Fig. 4 shows the results obtained by means of Raman spectroscopy. The acquired spectra were compared with the reference spectra of Antlerite (RRUFF ID: R110045) and Brochantite (RRUFF ID: R060133) from the RRUFF database identifying peaks at 415.52, 484.99, 987.86, 3489.83, and 3579.29 cm^-1. These results are in agreement with the ones obtained by the investigation performed with the XRD and confirm the presence of Antlerite $(Cu_3(SO_4)(OH)_4)$.

C. Photogrammetry 3D survey

Photogrammetry allowed one to construct the 3D model of the sculpture in order to perform a complete documentation of its conservation state.

Initially, the images were aligned and the dense cloud of points and the mesh were produced with a medium-quality. This first step was necessary in order to identify the markers automatically on all the images and to adjust their position when necessary (Fig. 5a). Afterwards, only the region of interest was selected and the scaled model was reconstructed at the highest possible quality and then the texture was applied.

The images were processed in separate chunks, corresponding to the different acquisition rings. Eventually, the chucks were aligned and merged to form the final model.

The scaled 3D model can be used by curators to perform measurements without the need of having the real object available. Moreover, it is possible to export the results as a video sequence, in order to display the results in a more user-friendly way both for curators or museum visitors [12].

IV. CONCLUSIONS

In this paper an example of a long term and multi-analytical monitoring applied to a bronze sculpture is reported. In fact, only through a monitoring over time it is possible to develop a tailored preventive conservation project. EIS measurements allowed to study the corrosion phenomena in progress, defining the stability and protective power of the different corrosion patinas. Furthermore, portable Raman spectroscopy has proven to be a powerful technique for the characterization of corrosion products in order to correlate colour and chemical composition with the electrochemical behaviour. Finally, photogrammetry is a useful tool to fully document the conservation state of a work over time.

This kind of approach was applied to other works of art belonging to the collection and it can be extended to other situation in which an in-situ monitoring campaign is necessary.

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