2023 IMEKO TC-4 International Conference on
Metrology for Archaeology and Cultural Heritage
Rome, Italy, October 19-21, 2023

Novel, effective and safe coatings for the protection of copper-based artefacts

Francesca Boccaccini[1,2], Aurelio Barbetta[1], Elena Messina[1], Marianna Pascucci[1], Cristina Riccucci[1], Gabriella Di Carlo[1]

[1] *Institute for the Study of Nanostructured Materials, National Research Council (ISMN-CNR), SP35d, 9, 00010 Montelibretti (Rome), Italy*
[2] *Department of Earth Sciences, Sapienza University of Rome, Piazzale Aldo Moro, 5, I-00185 Rome, Italy*

Abstract
Degradation processes in cultural heritage metal artefacts represents a critical issue since they can irreversibly compromise the conservation status of valuable works of art. The protective materials commonly used to hinder these processes are based on harmful or toxic corrosion inhibitors and solvents. Moreover, large amounts of organic solvents are typically used by conservators for their application and removal. In the last decades, the search for new materials that can simultaneously satisfy protective, aesthetic and safety requirements is receiving increasing attention.
In this contest, we have focused our attention on the development of sustainable polymer coatings that can provide an active protection and that are easy to be applied and removed using water-based solvents. A green polymer from renewable sources, such as chitosan, was selected and functionalized with anticorrosive species. Validation tests were performed on model copper-based substrates with different composition and surface finish. The performances were compared with a commercial benchmark.

I. INTRODUCTION

Copper-based artefacts are unique and valuable objects, that are part of our cultural heritage and has to be preserved from dangerous degradation processes. The composition and the surface finish of these objects can be very different depending on the aesthetic properties that the artist want to create. These features have an effect on the physico-chemical stability of the objects and their conservation needs.

In the modern museum collections, it is possible to find bronze sculptures with a very shiny surface, with a rough surface, with decorative elements and other ones with patinas, created by the artists or naturally grown. In particular, the patinas, that naturally grown on copper-based alloys, can have a complex chemical composition depending on several parameters, such as alloy composition, metallurgical features and environmental conditions [1-10]. The degradation processes occurring at the metal surface lead to the formation of alteration products and reactive compounds, such as oxides, carbonates, chlorides, hydroxychlorides, nitrates, sulphides and sulphates [1-4]. Among these species, particular attention has to be paid to chlorides, which in the presence of moisture and oxygen, are extremely harmful since they are responsible for a cyclic copper corrosion process. This degradation process can promote the conversion of metallic copper in a greenish powder of copper hydroxychlorides and can significantly compromise the conservation status of valuable works of art. However, depending on the environmental conditions around the metal object, stable degradation products can be also formed on the metal substrate thus creating a passive protective layer, known as “noble” patina. Therefore, both the chemical composition of the metal alloy and the exhibition/storage environment affects the surface reactivity of the artefacts. All these aspects have to be considered in the identification of the most appropriate conservation materials and methods.

The reliable conservation of contemporary copper-based works of art, including objects with shiny, rough and patinated surface, is a major challenge for conservators and scientists.

Nowadays, the most widespread approach for the corrosion protection of metal artefacts is their treatment with corrosion inhibitor molecules that chemically stabilize the metal substrate providing a chemical protective action. Several molecules have been investigated as active species and among them the heterocyclic compounds containing nitrogen have attracted much attention. In particular, the benzotriazole (BTA) is the most effective and widely used corrosion inhibitor that forms a stable layer by complexing with copper ions. Nevertheless, it is not always effective and it is toxic. There are many issues for what concerns its handling and leaching in the environment [11-12].

According to the literature [13], several classes of materials and strategies have been explored. Coatings based on waxes, acrylic resins, nitrocellulose lacquers, fluoropolymers, carboxylates, organosilanes compounds and other materials have been investigated. In addition to the protective properties, the coatings designed for cultural heritage applications have to preserve the colour of the original surface. Moreover, the protective treatments have to be reversible, thus avoiding any irreversible modification of the treated metal surface.

At present, the commercial products used for the conservation of modern copper-based works of art typically consist of the commonly used BTA, as corrosion inhibitor, dispersed into an acrylic resin or a microcrystalline wax. These products are usually effective but there are still many drawbacks to overcome due to the toxicity of the inhibitor and in particular the large amounts of harmful organic solvents that are necessary for their application and removal. Moreover, changes in appearance, as "plastic" effects or opacity, that are relevant in modern artefacts with shiny surface finish, have to be avoided. A long-term efficiency of the conservation materials and safe application and removal protocols are also necessary.

In this context, we have focused our attention on the development of novel polymer coatings able to provide an active protection of copper-based works of art and easy to be applied and removed by using non-toxic solvents, such as water and ethanol. A green polymer from renewable sources, such as chitosan, was selected as main component of the coating and it was used to embed the corrosion inhibitors. Chitosan is a biodegradable, biocompatible and abundant polymer which is commercially produced by deacetylation of chitin, the structural element in the exoskeleton of crustaceans, such as crabs and shrimp. Moreover, chitosan has high film forming capability, high transparency and can be dissolved in aqueous solutions. Due to all these properties, chitosan is widely used for several applications, as the development of edible coatings and biomedical uses, whereas its application for the conservation of cultural heritage is innovative and was explored in the last years [14-18].

In order to optimize the chitosan-based coatings, we have selected and prepared representative model substrate that were used to assess the protective efficacy of the developed coatings. Moreover, appropriate validation procedures have been identified and used to achieve information on the protective efficacy of chitosan-based coatings.

II. RESULTS AND DISCUSSION

A. Selection and preparation of model substrates

For the assessment and optimization of corrosion inhibiting materials, it is necessary to select and prepare sacrificial copper-based alloy substrates with chemical composition and metallurgical features similar to those of modern works of art. The use of appropriate metal substrates allows to study the behaviour of the protective coatings before their application on unique and valuable works of art.

The selection of the composition of the model substrates has been carried out on the basis of literature data obtained from the analysis of several modern bronze sculptures [1-3] and of selected modern case studies. According to the literature [1-3], valuable modern artefacts, such as from Rodin, Epstein, Herbert, Giacometti, etc., have been truly characterized to get information about the composition of the metal alloy and surface patina. The results have shown that the investigated copper-based alloys contain different amounts of alloying elements, mainly Sn, Zn and Pb. Therefore, within this study, we have selected a quaternary copper-based alloy (Cu-Sn-Zn-Pb, 555 alloy), with nominal composition of 85% Cu, 5% Sn, 5% Pb, 5% Zn and produced by casting, as representative of modern copper-based works of art. The metallurgical structure and chemical composition of the selected 555 alloy were investigated by SEM-EDS. A representative SEM image in Fig. 1 confirms that the selected alloy has a dendritic structure which is typical of cast bronze artefacts. The EDS spectra in Fig. 1 clearly show that the white islands mainly consist of Pb.

In addition, we have prepared a ternary copper-based alloy (CNR128, Cu-Sn-Pb) consisting of Cu 92.8 wt%, Sn 6.8 wt% and Pb 0.2 wt% (Fig. 2). This alloy has been also used as a more simple system to assess the protective efficacy of selected coating formulations.

Three different polishing procedures have been identified in order to tune the surface roughness of the reference copper-based disks over a wide range of roughness values which can be considered as representative of the variability of the real works of art. In order to obtain a flat and smooth surface with a mirror-like finish, the bare alloy disk was polished by using the SiC abrasive paper with P1200 grit and then by using two diamond pastes with particle size of about 9 and 3 μm. The so-obtained disk was labelled as 555-SF1.

To increase the surface roughness, the bare 555 alloy disk was polished by sequentially using two SiC abrasive papers with P1200 and P2500 grits, without using the ultimate finishing with diamond pastes (555-SF2). The surface roughness was furtherly increased by polishing the disks only using the SiC abrasive paper with P1200 grit (555-SF3).

The photographs of the three alloy disks in Fig. 3 show that the surface finish can be significantly modified by changing the polishing procedure. The surface roughness of 555-SF1, 555-SF2 and 555-SF3 was quantified by atomic force microscopy obtaining mean values of 18, 120 and 215 nm, respectively. The roughness of CNR-128 alloy was comparable to that of 555-SF1.

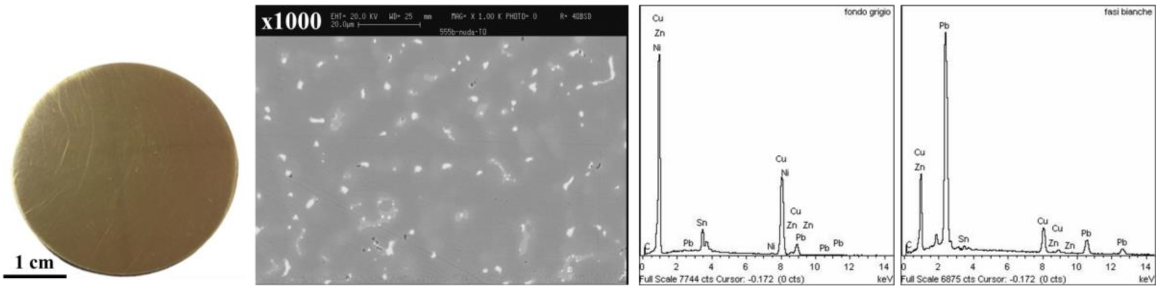

Figure 1. Photograph, SEM image and EDS spectra of bare 555 alloy. The EDS spectrum on the left was recorded on a large area and the one on the right on the white islands.

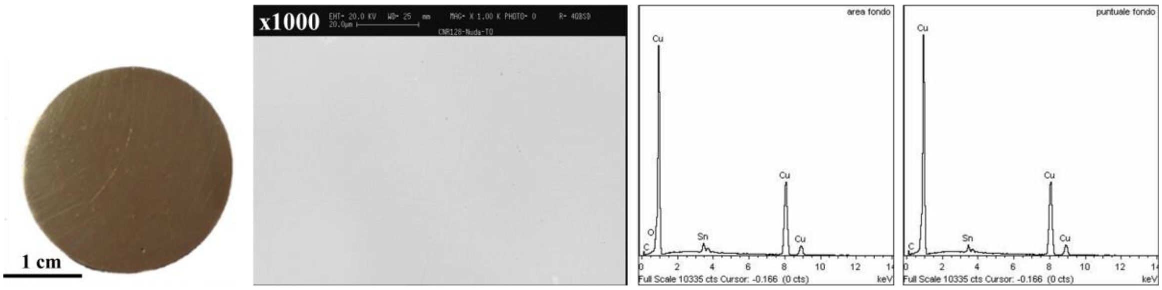

Figure 2. Photograph, SEM image and EDS spectra of bare CNR- alloy. The EDS spectrum on the left was recorded on a large area and the one on the right on the white islands.

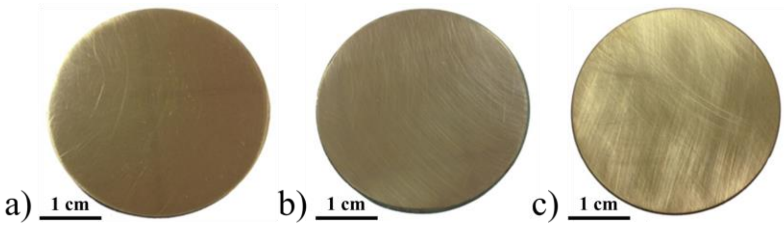

Fig. 3. Photographs of alloy disks with different surface roughness: a) 555-SF1, b) 555-SF2 and c) 555-SF3.

B. Optimization of validation tests

To assess the protective efficacy of polymer coatings, we have developed tailored procedures in order to investigate modifications at the metal surface after accelerated degradation treatments. Since chitosan coatings are mainly developed for indoor applications, we have developed appropriate procedures by using a more realistic environment with respect to the commonly used electrochemical tests with immersion in acidic solutions, also considering that water can dissolve these coatings.

In order to promote the corrosion of the alloy surface, the bare and coated alloy disks were treated with aggressive vapours. The accelerated corrosion treatments were carried out in a closed vessel in the presence of aggressive species, as HCl/water vapours, and slightly increasing the temperature in order to promote the corrosion processes and to rapidly get information about protective properties of the coatings [15].

C. Development of novel protective coatings and their assessment on model substrates

Chitosan-based coatings were optimized by taking into account the demanding protective, aesthetic and safety requirements that are necessary for cultural heritage applications. In particular, attention has been paid to the coating transparency and the use of safe procedures for their application and removal.

Chitosan solutions can be prepared using non-toxic solvents, as water and ethanol. However, it is necessary to use appropriate additives that improve chitosan solubility. This polymer is usually dissolved in dilute aqueous solutions at pH below 6 because of the protonation of the free amino groups [15].

With the aim of developing chitosan-based coating for corrosion protection of bronzes substrates, different corrosion inhibitors, such as the commonly used benzotriazole (BTA) and the less toxic mercaptobenzothiazole (MBT), were incorporated into the polymer matrix and their efficacy was investigate on the reference alloys, such as the CNR128 and the 555 alloy.

To evaluate the ability of chitosan-based coatings to inhibit the degradation of copper-based alloy substrates, accelerated corrosion treatments with acidic vapours were carried out. The results showed that both the chitosan-based formulations are able to inhibit degradation processes.

The optimized protective materials were also deposited on alloy disks with a high surface roughness, selected as another model substrate. In Fig. 4, some representative results obtained by optical microscopy show that the bare alloy disk is significantly degraded, whereas the one with chitosan-based coating is still stable and the formation of corrosion products cannot be detected.

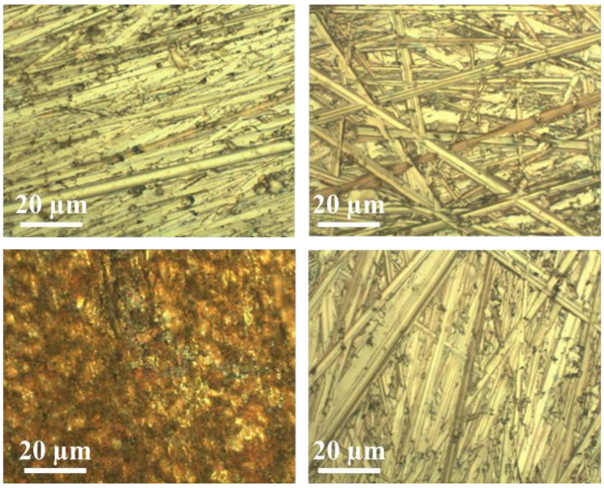

Fig. 4. Micrographs of the quaternary 555 alloy disks with a high roughness before (first row) and after (second row) corrosion treatments with HCl/H2O vapours for bare alloy (on the left) and coated with chitosan-BTA (on the right).

It is worth noting that chitosan-based coatings are transparent, colorless and completely removable.

III. CONCLUSIONS AND PERSPECTIVES

Our findings showed that chitosan-based coatings can be successfully used for the protection of bronze works of art stored or exhibited in indoor environments. Compared to commercial products as those based on acrylic resins and crystalline waxes, chitosan coatings provide promising protective and aesthetic properties. Moreover, they can be easily applied and removed from water-based solutions.

Further investigations are in progress to optimize chitosan-based coatings in terms of protective and aesthetic properties by using materials obtained from renewable natural sources or recycled waste.

ACKNOWLEDGEMENTS

The NANORESTART project (European Union's Horizon 2020 Research and innovation programme under the grant agreement no 646063) and the GREENART project (Horizon Europe research and innovation program under grant agreement no. 101060941) are acknowledged for financial support.

REFERENCES

[1] D.E. Couture-Rigert, P.J. Sirois, E.A. Moffatt, An investigation into the cause of corrosion on indoor bronze sculpture, Studies in Conservation, 57 (2012) 142-163.

[2] L. Robbiola, C. Fiaud, New model of outdoor bronze corrosion and its implications for conservation, ICOM Committee for Conservation, II (1993) 796-802.

[3] S. Bracci, A. Cagnini, M.P. Colombini, O.A. Cuzman, F. Fratini, M. Galeotti, D. Magrini, R. Manganelli del Fà, S. Porcinai, S. Rescic, C. Riminesi, B. Salvadori, A. Santagostino Barbone, P. Tiano, A multi-analytical approach to monitor three outdoor contemporary artworks at the Gori Collection (Fattoria di Celle, Santomato, Pistoia, Italy), Microchemical Journal, 124 (2016) 878–888.

[4] C. Chiavari, K. Rahmouni, H. Takenouti, S. Joiret, P. Vermaut, L. Robbiola, Composition and electrochemical properties of natural patinas of outdoor bronze monuments, Electrochimica Acta, 52 (2007) 7760-7769.

[5] L. Veleva, W. Farro, Influence of seawater and its aerosols on copper patina composition, Applied Surface Science, 258 (2012) 10072-10076.

[6] G.M. Ingo, T. de Caro, C. Riccucci, E. Angelini, S. Grassini, S. Balbi, P. Bernardini, D. Salvi, L. Bousselmi, A. Çilingiroglu, M. Gener, V.K. Gouda, O. Al Jarrah, S. Khosroff, Z. Mahdjoub, Z. Al Saad, W. El-Saddik, P. Vassiliou, Large scale investigation of chemical composition, structure and corrosion mechanism of bronze archeological artefacts from Mediterranean basin, Applied Physics A, 83 (2006) 513-520.

[7] K.P. FitzGerald, J. Nairn, G. Skennerton, A. Atrens, Atmospheric corrosion of copper and the colour, structure and composition of natural patinas on copper, Corrosion Science, 48 (2006) 2480-2509.

[8] O. Papadopoulou, J. Novakovic, P. Vassiliou, E. Filippaki, Y. Bassiakos, Chemical corrosion by chlorides on ancient-like bronzes and treatment by hydrogen glow discharge plasma, Appl Phys A, 113 (2013) 981–988.

[9] I. Constantinides, A. Adriaens, F. Adams, Surface characterization of artificial corrosion layers on copper alloy reference materials, Applied Surface Science, 189 (2002) 90-101.

[10] C. Soffritti, E. Fabbri, M. Merlin, G.L. Garagnani, C. Monticelli, On the degradation factors of an archaeological bronze bowl belonging to a private collection, Applied Surface Science 313 (2014) 762-770.
[11] D.A. Pillard, J.S. Cornell, D.L. Dufresne, M.T. Hernandez, Toxicity of benzotriazole and benzotriazole derivatives to three aquatic species, Water Res. 35 (2001) 557–560.
[12] Health Council of the Netherlands, 1,2,3-Benzotriazole. Health-Based Recommended Occupational Exposure Limit, (2000).
[13] M. T. Molina, E. Cano , B. Ramírez-Barat, Protective coatings for metallic heritage conservation: A review, Journal of Cultural Heritage 62 (2023) 99–113.
[14] M.S. De Luna, G. Buonocore, G. Di Carlo, C. Giuliani, G.M. Ingo, M. Lavorgna, Protection of bronze artefacts through polymeric coatings based on nanocarriers filled with corrosion inhibitors, AIP Conference Proceedings 1736, 020048 (2016).
[15] C. Giuliani, M. Pascucci, C. Riccucci, E. Messina, M. S. de Luna, M. Lavorgna, G. M. Ingo, G. Di Carlo, Chitosan-based coatings for corrosion protection of copper-based alloys: A promising more sustainable approach for cultural heritage applications, Progress in Organic Coatings 122 (2018) 138–146.
[16] F. Boccaccini, C. Giuliani, M. Pascucci, C. Riccucci, E. Messina, M.P. Staccioli, G.M. Ingo, G. Di Carlo, G. Toward a Green and Sustainable Silver Conservation: Development and Validation of Chitosan-Based Protective Coatings, Int J Mol Sci 23 (2022) 14454.
[17] E.Messina, C. Giuliani, M. Pascucci, C. Riccucci, M.P. Staccioli, M. Albini, G. Di Carlo, Synergistic Inhibition Effect of Chitosan and L-Cysteine for the Protection of Copper-Based Alloys against Atmospheric Chloride-Induced Indoor Corrosion, Int. J. Mol. Sci. 22 (2021) 10321.
[18] M.R. Caruso, G. D’Agostino, S. Milioto, G. Cavallaro, G. Lazzara, A review on biopolymer-based treatments for consolidation and surface protection of cultural heritage materials, J Mater Sci 58 (2023) 12954–12975.