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Editorial

Metals in Heritage Science

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1. Introduction

The valorization of our Cultural Heritage is deeply grounded in the study of the production, use and consumption of ancient metals. Modern analytical techniques allow us to obtain detailed information about the composition and microstructure of metal artifacts. This information is very useful for understanding historic materials and the manufacturing process. Moreover, the assessment of the state of conservation of metal objects allows us to detect degradation mechanisms and establish suitable conservation strategies for the safeguarding of Cultural Heritage.

In this framework, this Special Issue 'Metals in Heritage Science' includes original research and a review that cover the new achievements in the study of the composition, technological process, microstructure and deterioration phenomena of metal alloys, with a special focus on the use of the most recent analytical techniques and instrumentation for investigating the history of metal technology. Finally, innovative conservation and restoration solutions are also considered.

2. Contributions

This book presents a collection of manuscripts from cutting-edge academic researchers and consists of the following: (i) one review paper regarding fractographic, metallographic and chemical analyses as key tools for improving the interpretation of damage in historical copper and silver alloys [1]; (ii) six experimental research papers focused on the chemical and metallurgical characterization of ancient artifacts such as ceramic casting molds, Nuragic bronze objects, Renaissance swords, Japanese metallic threads and an emblematic copper-based alloy monument [2–7]; (iii) two research articles on the use of oxygen depletion testing for quantitatively measuring the deterioration of historical metals and on the employment of different portable/transportable devices to assess the effects of the bronze disease phenomenon [8,9]; (iv) one experimental research paper that aims to determine the optimal application conditions of a new multifunctional coating containing Ag-doped TiO_2 nanoparticles, when used as a possible protective agent for sandstone [10].

The review of Oudbashi and Wanhill [1] provides a very comprehensive survey of the long-term corrosion- and microstructurally-induced embrittlement of copper and silver alloys. Specific attention was paid to the analysis and interpretation of fracture surfaces in support of metallographic and chemical investigations. In this regard, several examples were supplied by the authors to prove the reliability of fractography as a diagnostic technique; notable instances are those related to the influence of residual stresses and burial-induced stresses in thin-walled hollow artifacts on stress corrosion cracking (SCC). Moreover, the evidence of damage consistent with SCC further underlines the significance of the burial environment. In fact, graves represent burial scenarios resulting in high local salinity, which is able to promote SCC in many classes of alloys. Finally, with the aid of these case studies, actual and potential remedial procedures were proposed by the same authors for restoring corroded and broken objects.

Concerning the chemical and metallurgical characterization of ancient artifacts, the first relevant contribution was proposed by Zhushchikhovskaya and Buravlev [2]. The

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article examined a unique assemblage of ceramic casting molds, discovered at one of the sites from the Bohai period (698–926 CE) in the territory of the southern Russian Far East, with the aim of identifying possible traces of metal alloys inside them. Nondestructive portable X-ray fluorescence (XRF) spectroscopy and scanning electron microscopy equipped with energy dispersive spectroscopy (SEM/EDS) were used for investigating a total of 34 samples (13 unbroken and minimally damaged artifacts and 21 fragmentary molds). On the carbonized surfaces of the molds, metals such as Cu, Sn, Pb and As were detected and interpreted as alloy components; in contrast, on the non-carbonized surfaces, no traces of the same elements were assessed. Based on the results, the authors assumed the employment of ceramic casting molds for manufacturing objects in multicomponent copper alloys such as Cu-Pb, Cu-Sn-Pb and Cu-Sn-Pb-As. This is in agreement with previously reported data for bronze items and metal residues from ceramic crucibles belonging to the Bohai period.

The contribution by Nocco et al. [3] proves the feasibility of a Monte Carlo simulation algorithm for X-ray interactions with matter in evaluating the chemical composition of corroded archeological bronzes (three daggers, a *Bronzetto* and a *Navicella*) from the period *Nuraghi* (1700–1200 BCE). In this work, independent Monte Carlo simulations were applied in an interactive and inverse manner. More specifically, an initial guess model was generated on the basis of the visual inspection of the samples and of any other information available prior to the simulations (e.g., results from Raman spectroscopy analysis). After each simulation, the model was updated until it matched the experimental spectra with a sufficiently low chi-squared error. The proposed methodology allowed us to obtain a near-perfect reproduction of the bulk composition without cutting, scratching or damaging the objects. A correlation between the chemical and geological data then enabled us to suggest a possible origin of the artifacts; through a comparison of the same data with those derived from catalogs, conclusions regarding the authenticity of the bronzes were reached. In [4], the aforementioned analytical technique was successfully applied by the same authors to three bronze miniatures of pilgrim flasks consistent with the Nuragic civilization and preserved at the *Antiquarium Arborense* Museum in Oristano (Italy). The research demonstrated that they were composed of Cu-Sn and Cu-Pb-Sn alloys; no zinc or traces of surface tinning were assessed, thus supporting the preliminary hypothesis of authenticity of all miniatures.

In ref. [5], two swords tentatively dating around 1480 to 1490 CE and coming from the 'Luigi Marzoli' Arms Museum in Brescia (Italy) were investigated to gather some information about their manufacturing process and provenance. Both items can be classified as swords 'alla veneta' (or Venetian type) due to the presence of the following peculiar features, aimed at improving the grip and making the hilt more ergonomic: (i) branches on the two edges of the blades to support the index and middle fingers of the hand; (ii) a knuckle-guard that departs from the center of the quillon and reaches the pommel; (iii) single or double-edged blades with a lenticular section. The microstructural characterization proved the coexistence of different ironmaking processes (i.e., direct and indirect processes) as well as the employment of various heat treatment routes (for example water, oil or air quenching and tempering) for manufacturing the single parts of the objects. The parts were then joined together with a copper alloy (provided in the form of chips or grains) to improve their cohesion. These findings are supported by previously reported evidence such as the presence of a 'canecchio' furnace in Venetian areas during the diffusion of the ergonomic hilts and the ascertained use of finery iron for manufacturing armors.

The contribution by Geminiani et al. [6] contains the results of an experimental campaign on metallic threads in the form of thin strips from different parts of six Japanese samurai armors dating back to the 15th to 20th century and belonging to 'Museo delle Culture' (Lugano, Switzerland). The research allowed us to assess the coexistence of traditional and modern production techniques as well as of traditional and modern materials. With regard to traditional manufacturing, it was demonstrated that the support for the strips consisted of paper treated with alum salts, while the adhesives were animal glue, rice starch or *urushi* (a natural polymeric material, offering protection from oxidation and extra-resistance against blades). Clay and gypsum were admixed with the adhesive and spread under the threads or on their surfaces probably to attain special effects. An evolution over the centuries in the use of metals was also highlighted: between the 17th and 19th century, silver and gold alloys and orichalcum (a copper–zinc alloy) were adopted to realize gilt strips, whereas since the Meiji period (1868–1912 CE), aluminum was preferred for both gilt and silver coloring. Starting from the 20th century, the same aluminum together with rayon and an industrial metallic thread named "Cellometal" (i.e., an Al strip coupled with a cellophane foil) have been extensively used for reducing costs. Finally, a very surprising result by the authors was the employment of tin foil, which has not been reported in the literature before; it was suggested that its use was due to the intention of providing the armors with a russet iron appearance.

In ref. [7], the outdoor sculpture of the king D. Afonso Henriques (1109–1185 CE) in Guimarães (North Portugal) was studied to collect historical data and technical information about its elemental composition and corrosion products. A multi-analytical approach consisting of XRF, X-ray diffraction (XRD), optical microscopy (OM) and SEM/EDS was considered. Based on the results, the monument was produced by the sand-casting technique and it was made of a Cu-Sn-Zn ternary alloy containing Pb, Fe, As, Bi and Mn as minor alloying elements. This composition was consistent with that of previously reported castings produced in Europe from the 18th to the early 20th century. Stable corrosion products, such as brochantite, were also detected on the surfaces of the sculpture; it should be noted that these natural patinas were able to supply a passive layer that protected the underlying material from the atmosphere. Finally, the main findings of this work represented the first step for applying suitable conservation strategies to monuments with similar features.

The articles by D. Thickett [8] and D. Porcu et al. [9] contain recent results on the use of oxygen depletion testing for quantitatively measuring the deterioration of historical metals and on the employment of different portable/transportable devices to assess the effects of the bronze disease phenomenon. The first article [8] examines several metal objects obtained from a number of excavations, which were monitored through oxygen depletion tests. During the tests, each artifact was placed into a sealed jar under relative humidity and pollutant gas controls; any decrease in oxygen concentration was then measured and correlated to the deterioration rate. The experimental findings proved that oxygen depletion tests gave good quantitative measurements of corrosion as corroborated by both visual comparison and weight-loss measurements by linear stripping voltammetry or chemical stripping for copper, lead and steel but not for silver. In addition, the second article [9] examines two sets of bronze/silicon bronze samples, which were considered to be representative of Florentine Renaissance artworks and modern works of art. All specimens were artificially aged and analyzed by Raman spectroscopy, fiber optics reflectance spectroscopy (FORS) and spectral domain optical coherence tomography (SD-OCT) with the aim of early identifying and stabilizing reactive copper chloride (CuCl) and removing the harmful corrosion products (atacamite and polymorphs). The obtained results showed the effectiveness of Raman spectroscopy in detecting green compounds such as atacamite, whereas the ability of FORS to identify basic copper chlorides was verified in zones with high concentrations of analyte. The authors also demonstrated the capability of the SD-OCT technique to recognize incoherent and powdery corrosion layers, together with its efficiency of collecting stratigraphic information on the patinas, generally based on micro-sampling.

Finally, the main objective of the research by Chobba et al. [10] was to determine the optimal application conditions of a new multifunctional coating containing Ag-doped TiO_2 nanoparticles (NPs) when used as a possible protective agent for sandstone. These NPs with anatase structures, spherical shapes and controllable sizes were fabricated using the sol–gel method. Their biocidal activity was investigated by comparing their performance to pure TiO_2 nanoparticles against two representative Gram-positive and -negative bacterial strains, under visible irradiation and in the dark; the antimicrobial efficiency of different contents of NPs (0.1–1 mol%) was also evaluated against two phototrophic strains isolated from deteriorated surfaces. The prepared nanopowders were then dispersed in a binder with different powder/binder ratios (0.1, 0.2, 0.5 and 1% *w*/*v* TiO_2) and subsequently applied in different amounts (2, 3 and 6 g/m^2) on Serena stone specimens. The experimental findings suggested that the photoactivation and photokilling activity of TiO_2 were increased by the addition of Ag. Moreover, it was concluded that the application of 2 g/m^2 nanocomposite at powder/binder ratios equal to 1% *w*/*v* TiO_2 provided a fine hydrophobic character for the stone material with admissible chromatic variations.

3. Conclusions and Outlook

The Special Issue delves into the latest research on the composition, technological process, microstructure and deterioration phenomena of historic metal objects. The review and the papers demonstrate that an in-depth study of the ancient artifacts is still highly relevant for establishing suitable conservation and restoration solutions for the safeguarding of our Cultural Heritage.

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