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Large scale investigation of chemical composition, structure and corrosion mechanism of bronze archeological artefacts from Mediterranean basin

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ABSTRACT A large number of Cu-based archaeological artefacts from the Mediterranean basin have been selected for investigation of their chemical composition, metallurgical features and corrosion products (i.e. the patina).

The guidelines for the selection of the Cu-based artefacts have taken into account the representativeness of the Mediterranean archaeological context, the manufacturing technique, the degradation state and the expected chemical composition and structure of the objects.

The results show wide variation of the chemical composition of the alloys that include all kinds of ancient Cu-based alloys such as low and high tin, and also leaded bronzes, copper and copper-iron alloys.

The examination of the alloy matrix shows largely different metallurgical features thus indicating the use of different manufacturing techniques for producing the artefacts. The results of the micro-chemical investigation of the patina show the structures and the chemical composition of the stratified corrosion layers where copper or tin depletion phenomenon are commonly observed with a remarkably surface enrichment of some soil elements such as P, S, Ca, Si, Fe, Al and Cl. This information indicates the strict interaction between soil components and corrosion reactions and products. In particular, the ubiquitous and near constant presence of chlorine in the corrosion layers is observed in the patina of the archaeological Cu-based artefacts found in different contexts in Italy, Turkey, Jordan, Egypt, Spain and Tunisia. This latter occurrence is considered dangerous because it could induce a cyclic corrosion reaction of copper that could disfigure the artefact.

The micro-chemical and micro-structural results also show that another source of degradation of the bronze archaeological artefacts, are their intrinsic metallurgical features whose formation is induced during the manufacturing of the objects, carried out in ancient times by repeated cycles of cold or hot mechanical work and thermal treatments. These combined treatments induce crystallisation and segregation phenomena of the impurities along the grain boundaries and could cause mechanical weakness and increase the extent of the inter-granular corrosion phenomena.

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1 Introduction

The development of innovative and tailored strategies and products for the long-term stable conservation of archaeological Cu-based artefacts needs to identify the origin of degradation phenomena and its relationship with the archaeological environment.

In the framework of the EFESTUS project (financially supported by the European Commission, INCOMED contract no. ICA3-CT-2002-10030), archaeological areas of the

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Mediterranean basin and well-defined and coherent groups of Cu-based value artefacts found there, have been selected in order to study degradation cases, representative of the different possible Mediterranean deterioration phenomena.

The guidelines for selecting artefacts have also considered their use, manufacturing technique, expected chemical composition and metallurgical structure as well as the soil nature.

This approach is justified considering that the data basis currently available from literature [1–5], in many cases it is only a juxtaposition of results obtained by adopting different analytical and methodological approaches and by studying large numbers of individual artefacts of all kinds, not related to archaeological contexts or to the intrinsic metallurgical or chemical features of the artefacts [1–4].

In some cases, phenomenological models have been also proposed and classes of corrosion structures were defined in order to explain the formation of the corrosion layers, even though some deviations and discrepancies have pointed out by the same authors [5].

With these consideration in mind, archaeological contexts and Cu-based artefacts found there have been selected as representative of the different Mediterranean situations, and have been studied by systematically using the same methodological approach and analytical techniques.

The latter include: scanning electron microscopy combined to energy dispersive spectrometry (SEM-EDS), optical microscopy (OM), X-ray diffraction (XRD), inductively coupled mass spectrometry (ICP-MS) and atomic absorption spectrometry (AAS).

The complete description of the archaeological contexts and the chemical, micro-chemical and micro-structural results obtained from the more significant and representative 70 artefacts and 12 archaeological soils is reported in the EFESTUS project Anglo-Arabic Web Site (www.efestus.just.edu.jo).

2 Experimental

The chemical composition, corrosion product nature and microstructures were studied by X-ray diffraction (XRD), inductively coupled mass spectrometry (ICP-MS), atomic absorption spectrometry (AAS), optical microscopy (OM), scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS).

Both SEM and EDS characterisation were carried out by using a Cambridge 360 scanning electron microscope equipped with a LaB_6 filament and a four sectors back scattered electron detector. The samples have been coated with a thin layer of carbon in order to observe the samples without charging effects. The carbon coating was deposited by using an Emitech sputter coater K550 unit, a K250 carbon coating attachment and a carbon cord at a pressure of 1×10^{-2} mbar in order to produce a carbon film with a constant thickness of about 3.0 nm.

FIGURE 1 Archaeological Cu-based artefacts found during the excavation of Turkish, Jordanian and Italian contexts. The artefacts are a shield, raw pre-monetary materials used in Italy i.e. the so-called *Aes rude*, a helmet and a dagger (from the *top* to the *bottom*)

The surface morphology of the samples has been observed by using an optical microscope Leica MZ FLIII or a Nikon apparatus equipped with a digital camera.

OM investigation of cross-sectioned samples has been carried out by using a Leica MEF 4 microscope equipped with a digital camera. In order to prepare the cross sectioned materials, representative fragments of bronze artefacts were embedded in epoxy resin with a setting time of 24 hours and sectioned by using a diamond saw in order to preserve the corrosion products. The sections were polished with silicon carbide papers upto 1200 grit and the final polishing was performed with diamond pastes up to 1/4 μm in order to have mirror like surfaces on the sections.

X-ray diffraction patterns were recorded directly on the ancient bronzes, by multiple scanning using an automated Seifert XRD-3000 diffractometer. The identification of the species was carried out by using a Seifert 3000 Software Index I.

3 Results and discussion

In Fig. 1, some of the selected Cu-based archaeological artefacts are shown.

The selected artefacts have been recently found during the excavation of 12 archaeological areas representative of possible different Mediterranean contexts. These latter include desert areas in Jordan, Tunisia and Egypt, continental sites, corrosive marine environments located on coastal areas (S. Antioco and Tharros, Sardinia, Italy) and the riverbanks of a very big ancient city such as Rome. We have considered also Carthage (Tunisia) that was the most important Punic city, and the Anatolian city of Ayanis (VII cent. BC) whose fortress has an altitude of 1866.00 m above sea level, and where snow usually stays on the fortress for 5 or 6 months.

The soils of the archaeological contexts have been sampled and analysed. The results have been reported in the Reports and Deliverables for the European Commission [6] and also in the EFESTUS project Anglo-Arabic Web site (www.efestus.just.edu.jo).

It is worth noting that the selected Cu-based archaeological artefacts have been produced by using the main manufacturing techniques employed in ancient times to produce bronze artefacts and includes casting in moulds, lost wax casting, minting, and cold and hot mechanical shaping. The ancient use of selected archaeological artefacts was different being artistic, ritual, common use objects, coins, weapons, cosmetic tools, mirrors and jewels.

Their chemical composition is very wide and includes all kinds of the ancient Cu-base alloys such as copper, low tin and high tin also leaded materials and Cu-Fe alloys.

The chemical composition of the bulk metal of the 70 most representative selected artefacts are reported in Fig. 2 as histograms of the frequency distribution of Cu, Sn, Pb and Fe.

In order to provide evidence of the wide variation of chemical composition of the selected artefacts in the latter figure, the frequency distribution of a nearly equivalent number of Punic coins, of the same series, and found in the same archaeological context in Sardinia [7–9], is shown on the right side of the figure.

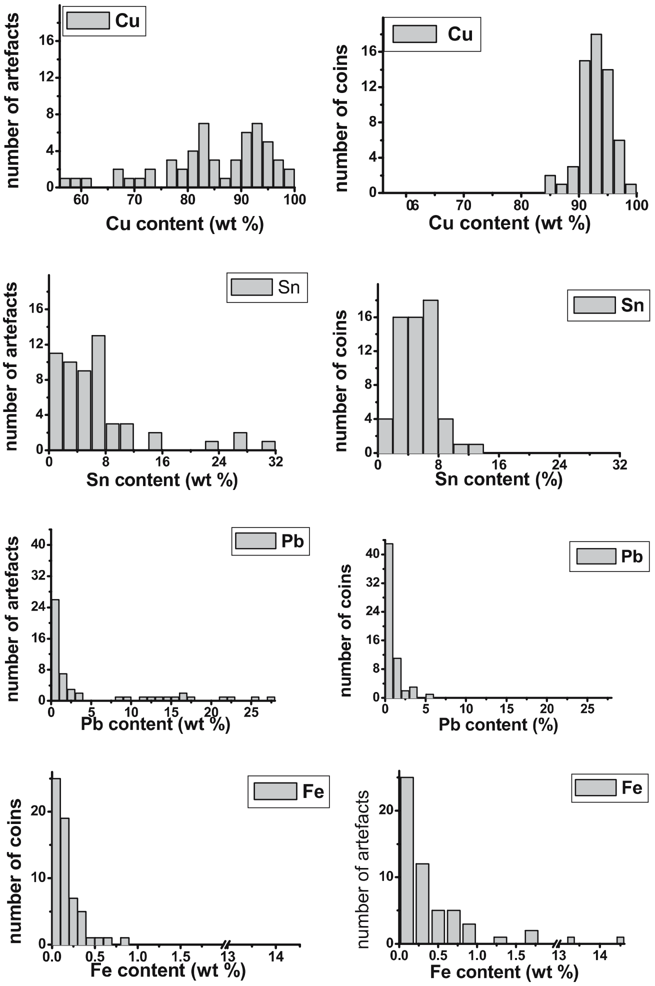

FIGURE 2 Frequency distribution of Cu, Sn, Pb and Fe content for the selected bronze artefacts found in different archaeological areas of the Mediterranean basin and for a nearly equivalent number of bronze Punic Coins of the same series, found together in the same archaeological excavation in Sardinia (Italy), *left* and *right* column, respectively

The histograms relative to the EFESTUS archaeological artefacts reported in Fig. 2 show a very large variation of the content of the alloying and minor elements.

Copper is the main component of all the archaeological alloys that in some artefacts can be assigned to the leaded bronzes class because the Pb content ranges from 6–8 weight percent (hereafter wt.%) to about 27 wt. %.

Tin is present in largely different amounts in all the samples and varies from 0.5 wt. % to 31 wt. %. The wide variation of the tin and lead content indicates the tailored use of different materials to produce artefacts to be differently utilised.

Tin is the main alloying element for producing bronze and its increasing amount consequently increases the mechanical properties of the bronze even though, the Sn content generally does not exceed the 8–10 wt. %, as also evidenced by the results shown in Fig. 2. Indeed, bronzes containing much more 10 wt. % cannot be satisfactorily worked without some danger of breaking, due to the formation of the hard and brittle $(\alpha + \eta)$ eutectoid phase in the bronze.

Lead is a common addition to bronze carried out in antiquity for producing objects characterised by low mechanical properties to be utilised at room temperature. Indeed, an addition of lead up to 2% improves the fluidity of the melted bronze alloy [10, 11] even though, a loss of mechanical properties could be induced, and if the lead amount is increased up to 3–4 wt. %, hardness and toughness are consequently reduced. With higher amounts of Pb, a remarkably deterioration of mechanical properties is produced and the only derived advantage is the low cost of lead with respect to the more expensive and rare tin. The loss of mechanical and thermal features is well explained by the copper-lead diagram. Indeed, because lead has substantially no solid solubility in copper and copper-based alloys, if the percentage of lead in bronze is higher than a few percent (pct), lead occurs as a dispersion of fine particles throughout the bronze [7–9].

The number of the lead particles and its distribution as globules in the copper matrix vary as a function of the lead content and casting parameters thus giving rise to the formation of a material constituted by a copper matrix where lead islands are scattered.

The resulting effect of the presence of lead on the microstructure of the bronze artefacts, can be seen in Fig. 3, where a back scattered electrons image of a cross-sectioned low-leaded bronze Punic coin is shown.

From a compositional point of view, the lead data reported in the histogram of Fig. 2, are comparable with the chemical composition of the Etruscan, Greek and Italic bronze objects, and with the small amount of literature data concerning the lead content of the Phoenician-Carthaginian artefacts from Spain [7–11], whereas the Sardinian items have generally a lower lead content [10, 11].

Another common trace or minor element in Cu-based artefacts is iron, which is mainly present with copper as copper-iron sulphides (see ED spectrum D of Fig. 3) or as an iron oxide. This element could come from the impure copper ore or from the fluxing compounds used during the smelting process

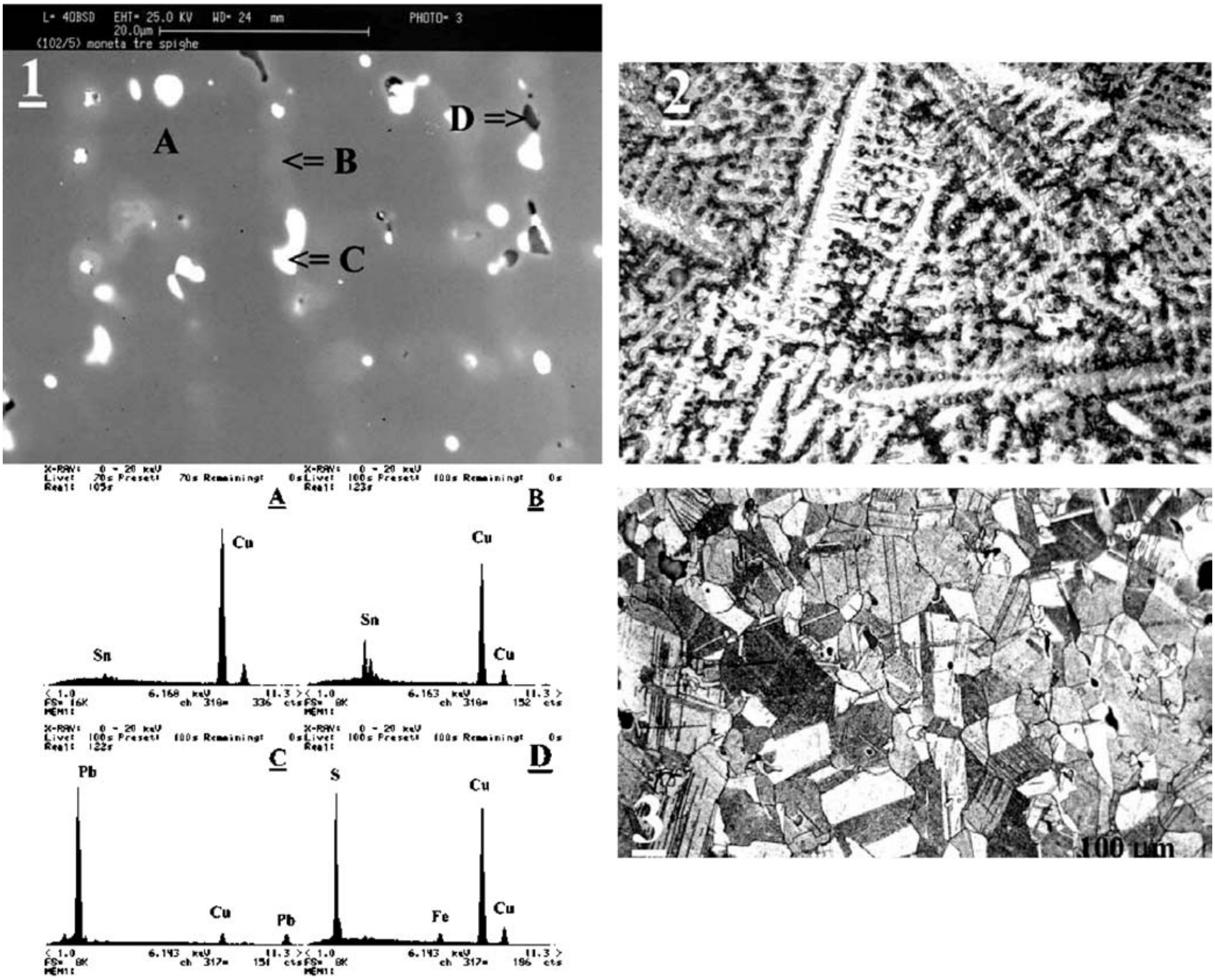

FIGURE 3 Cross-sections of bronze archaeological artefacts found at Tharros (Sardinia, Italy), image 1 and 2 and cross-section of an object found at Ayanis (Van, Turkey). The images show typical examples of the different metallurgical features observed in the EFESTUS Cu-base selected archaeological artefacts. In the dendritic matrix [back scattered electron (BSE) image 1 and optical image 2] small scattered lead islands and Cu-Fe sulphides (ED spectrum C and D of image 1, respectively) are present. Tin inverse segregation phenomenon has also occurred in the dendritic structure as shown by the ED spectrum B of image 1. The image 3 shows a well-crystallised matrix characterised by the presence of twinned grains with different size and slip lines

and as pointed out by Craddock [10, 11] the iron content could be used as technological indicator of the smelting process.

An amount of about 0.05 wt. % is typical of the early processes carried out under poor reducing conditions, while content higher than 0.3 wt. % indicates a more efficient process and therefore, the iron content could evidence the advanced technological competency and skill of the smelting operator.

Also for iron, the EFESTUS results are comparable with those obtained from bronze Etruscan, Greek and Roman objects [10, 11], except only for few Punic coins found in Sardinia which have a relevant content of iron associated in some cases with a low amount of cobalt.

As for silver (not shown in Fig. 2), the results indicate how its variation is within narrow limits from 0.007 wt. % and 0.18% and that artefacts with a lead content higher than 2 wt. % have generally a low silver amount ranging from 0.007 wt. % to 0.05 wt. %.

On the contrary, the artefacts with a silver content ranging between 0.05 and 0.18 wt. % are characterised by a lead content lower than 2.0 wt. %. This result suggests that silver comes more likely from the copper ores than from the added lead, as already suggested by Giumlia-Mair [12].

The zinc content (not shown) ranges from 0.01% to 0.96 thus indicating the use of copper ores with variable content of zinc sulphide.

The arsenic (not shown) and antimony amount of the EFESTUS artefacts varies from 0.01 wt. % to 0.62 wt. % and 0.01 wt. % to 0.21 wt. %, respectively, thus confirming relevant differences in the alloying and refining practices. The arsenic and antimony amounts indicate that the copper has been obtained from the use of a sulphide ore, which was not completely roasted [10] and in some cases raw refining techniques.

The above reported results indicate the presence of variable amounts of impurities most of which could be reduced to acceptable levels [11] quite easily by melting the copper or the bronze in an open crucible and allowing the unwanted elements to oxidise, to float to the melted surface and be skimmed off. Therefore, the results indicate that refining processes have not always been carried out before casting, and that raw bronzes were used for producing many of the selected artefacts. Refined materials were used only for producing weapons such as shields, dagger and helmets that have been manufactured by utilising alloys with well-controlled chemical composition.

The metallurgical features of the selected artefacts have been investigated and some exemplary results are shown in Figs. 3 and 4.

The images 1 and 2 displayed in Fig. 3 have been obtained from a Punic coin and an arrowhead and show a dendritic matrix typical of as cast artefacts. In the matrix, small scattered lead islands and Cu-Fe sulphides (ED spectrum C and D of image 1, respectively) are present. Furthermore, tin inverse segregation phenomenon has also occurred in the dendritic structure as shown by the ED spectrum B related to the image 1.

The image 3 shows another example of the typical structure of well shaped artefacts obtained via repeated cycles of mechanical working and hot treatments, a well-crystallised matrix is present, and is characterised by the presence of twinned grains with different size and slip lines.

In Fig. 4, an uncommon example of ancient metallurgical structure is shown: the micro-chemical structure of a cross-sectioned Aes rude found at Terrasebis (Sardinia, Italy). The back scattered electron (BSE) image and the ED spectra show the presence of circular to elliptical α-iron spheroids (spectrum B) scattered in the copper matrix (spectrum A). The white interdendritic phases consist of lead (spectrum C).

These unworked lumps of Cu-based materials i.e. Aes rude, have been found in many Italian archaeological sites and dated between the sixth and third centuries BC. Archaeological considerations indicate Aes rude have been appreciated as currency, as a medium of exchange and as a form of saving, and the micro-chemical investigation of these artefacts discloses their apparent unusable nature for any other functional applications or possible use. Indeed, Aes Rude appear as copper materials but micro-chemical results indicate that they consist of a highly ferruginous leaded copper and therefore, they are useless for producing other metal objects via casting or hot and cold working. Notwithstanding this intrinsic negative feature, the production of these intractable Cu-based alloys was deliberately carried out in ancient Italy for maximising the process yield in terms of produced metal from an impure and unselected metal ore by tailoring the smelting process parameters.

With these consideration in mind, the micro-chemical investigation of these ancient iron-copper alloys i.e. Aes rude, give evidence of the passage from the acceptance of an artefact value based on its true nature or potential use to the acceptance of the value based only on its appearance or form independently from its present or future use.

The large-scale characterisation has also documented the complex micro-chemical structure and nature of the corrosion products grown during the long-term archaeological burial, and has indicated that the artefacts suffer from an intense and selective dissolution of copper that in many cases induce the formation of a stratified structure, whose internal zone is mainly composed of cuprous oxide and copper chlorides. The results obtained in the framework of the EFESTUS project have also shown that the worked and shaped artefacts via thermo-mechanical treatments are heavier affected by the copper degradation induced by chlorine. The nature of corrosion products have been studied by means of XRD and the results have provided good insight into the corrosion layers.

XRD has shown the presence of copper and tin species such as romarkite (SnO), cassiterite (SnO_2), cuprite (Cu_2O), tenorite (CuO), carbonates such as malachite ($Cu_2(OH)_2CO_3$), azzurrite ($Cu_3(OH)_2CO_3$), smithsonite ($ZnCO_3$), leadlhillite ($PbSO_42PbCO_3Pb(OH)_2$) and cerussite ($PbCO_3$) as well as a complex copper-iron sulphide (calcopirite, $CuFeS_2$). The presence of atacamite ($Cu_2(OH)_3Cl$), nantokite (CuCl), brochantite ($Cu_4(OH)_6(SO)_4$), calcantite ($CuSO_45H_2O$) and piromorfite ($(PbCl)Pb_4(PO_4)_3$) has been also frequently monitored.

This information gives evidence that the outermost corrosion layers are formed also via the interaction between soil constituents (Cl, P, Si, Fe, Al, K, Ca, S, CO_2) and metal corrosion products mainly composed of copper whose amount on the artefact surface is often decreased by the long-term cor-

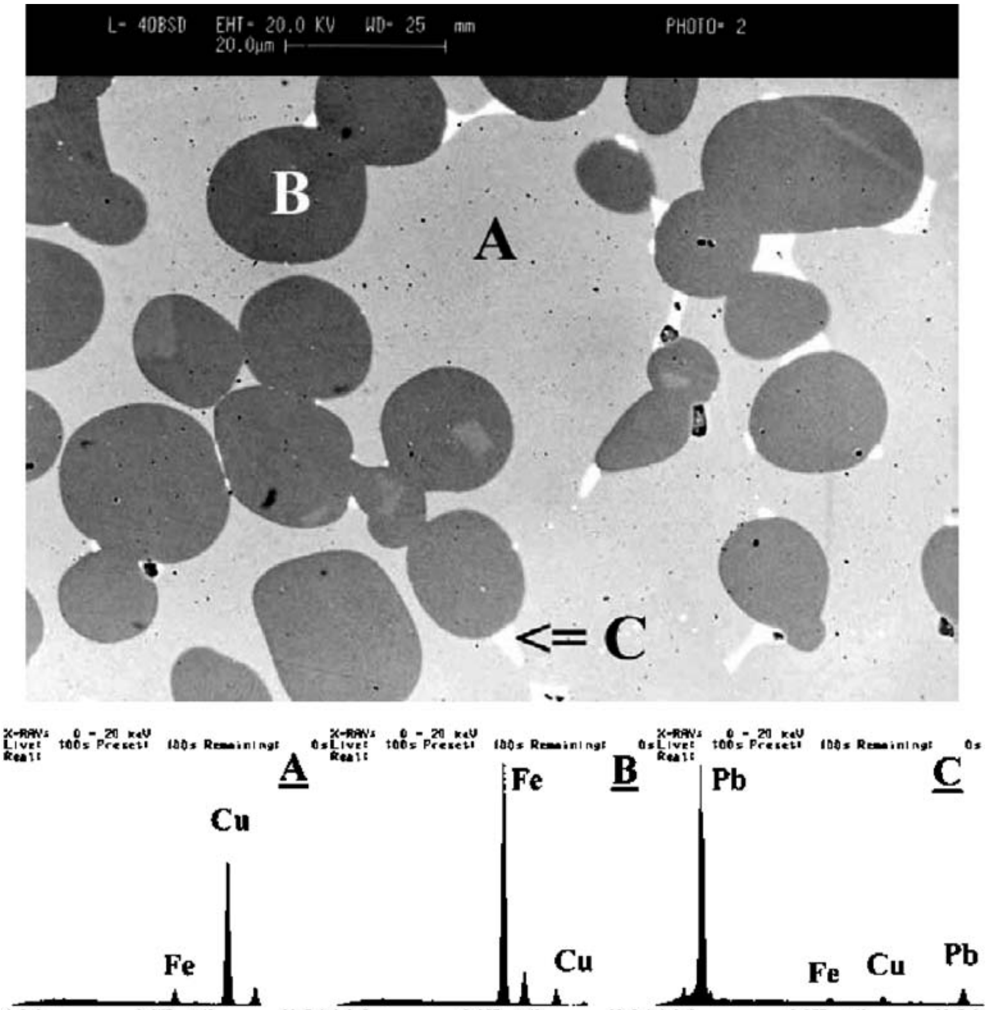

FIGURE 4 Micro-chemical structure of a cross-sectioned Aes rude found at Terrasebis (Sardinia, Italy). The BSE image and the ED spectra show the presence of circular to elliptical α-iron spheroids (spectrum B) scattered in the copper matrix (spectrum A). The white interdendritic phases are constituted by lead (spectrum C)

rosion. The presence of carbonates, chlorides, silicate, phosphate, sulphate and sulphides also enriched with Ca, K, Al and Fe demonstrate a strict interaction between soil constituents and artefacts corrosion products.

Some typical examples of corrosion product structures are shown in Fig. 5 where cross-sections of bronze archaeological artefacts found in Turkey and in Italy are reported. In particular, the images A and B show the metallurgical features and the nature of the corrosion products grown during the burial of a shield and a helmet, respectively, and image C shows the corrosion products structure of a Punic coin.

The micrographs taken by optical microscope (dark field observation) describe the complex nature of the stratified corrosion products: the dark spheroids, grains and thick layer consist of the surviving metal, the red crystals, rounded phases, erupting nodules or layers are cuprous oxide (cuprite, Cu_2O), the green compounds are Cu (II) carbonates or oxychlorides and the yellow-orange phase is cuprous chloride present at the interface between external corrosion products and metal relic.

Furthermore, images B and C of Fig. 5 describe the mechanism of the so called "bronze disease" which is a dangerous cyclic copper corrosion phenomenon induced by the exposure to air of the reactive cuprous chloride (CuCl) species located inside the archaeological artefact. Indeed, when cuprous chloride is exposed to the atmospheric humidity cyclically reacts with oxygen and the water coming from the humid atmosphere thus gives rise to the formation of the greenish $2Cu_2(OH)_3Cl$ (atacamite and its polymorphs) that reacts with copper to form new cuprous chloride and water. In this way copper, chlorine, oxygen and water are converted into cuprite (Cu_2O) and atacamite ($2Cu_2(OH)_3Cl$) in a cyclical and continuous process that can disfigure the archaeological object.

Cuprous chloride is formed during the burial via the interaction between copper and Cl^- anions coming from the soil. It is worth noting that large amounts of chlorine up to 22 mg/g have been monitored in the selected archaeological areas not only in the coastal sites of Sardinia but also in archaeological contexts located very far from the sea such as the desert areas of Jordan and the mountain of Ayanis (Turkey). Indeed, in very ancient times these latter areas were salty lakes and the soil is still heavily contaminated by the presence of chlorine.

The images B and C also show the protective role of the copper (II) compounds and of the cuprite (Cu_2O) layer that protects the surface, and impedes the interaction between cuprous chloride and water coming from the atmosphere, and therefore, the occurrence of the cyclical and continuous copper corrosion process. This information indicates that the con-

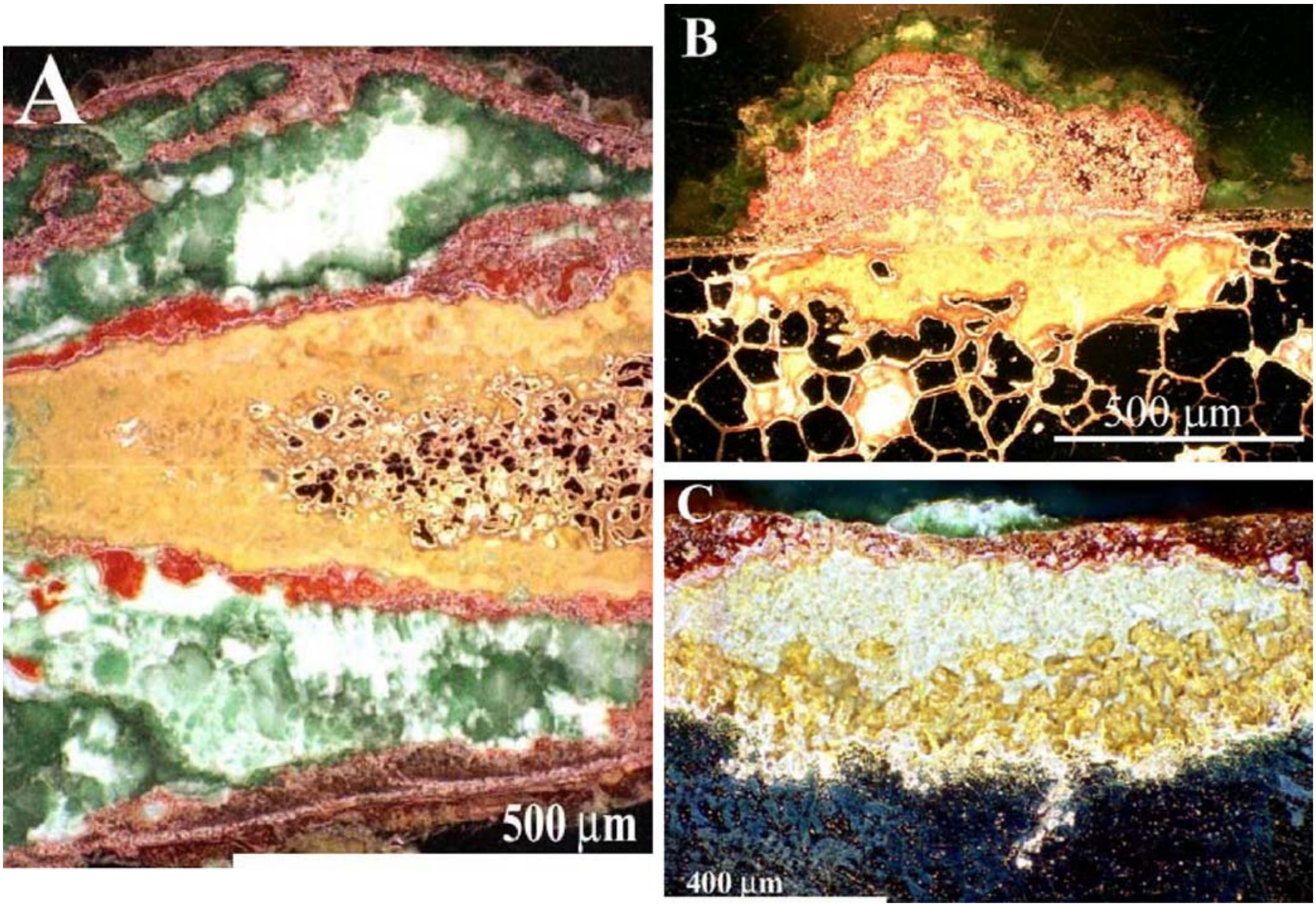

FIGURE 5 Cross-sections of bronze archaeological artefacts found at Ayanis (Turkey), image A and B, respectively which show the metallurgical features and the nature of the corrosion products grown on a shield and on a helmet. The image C shows the corrosion products structure of a Punic coin found at Tharros (Sardinia, Italy). The images taken by optical microscope (dark field observation) show typical examples of the metallurgical features and complex nature of the stratified corrosion products grown during the archaeological burial. The dark spheroids, grains and thick layer are consist of the surviving metal. The red crystals, and rounded phases or layers are cuprite (Cu_2O), the yellow-orange phases are copper chlorides, and the green compounds are Cu (II) carbonates or oxychlorides. Image B shows also the occurrence of heavy intergranular corrosion phenomena that preferentially attack the grain boundaries inducing the embrittlement of the artefact

servation materials and methods must locally inhibit the dangerous presence of chlorine and that a particular care must be used to avoid the removal of the protective corrosion product layers, and the contact between cuprous chloride and water and oxygen of the atmosphere.

In particular, the mechanical cleaning carried out for removing the external corrosion products, encrustations and the phases coming from the soil cannot ensure the complete removal of the corroding agents such as Cl, P and S, that could be yet present within the patina thus inducing a further degradation. Moreover, the above discussed results demonstrate that the removal of Cu (II) compounds and the cuprite (Cu_2O) layer from the surface could expose the copper chlorides present under the Cu_2O layer, thus inducing the cyclic reaction of copper corrosion and therefore, inducing the partial disfiguration of the artifact. Therefore, particular attention must be paid before and during the removal of surface encrustations and corrosion products layers in particular of cuprite in order to avoid to exposure copper chlorides to humidity and oxygen.

The role of the cuprite layer has been discussed by Lucey [13] and has been considered to be acting as an electrolytical membrane allowing the transport of anions such as Cl^- and O^{2-} inward and cuprous ions outward. Indeed, the presence of copper chlorides in the archaeological artefacts indicates a noticeable transportation of chlorides from the soil trough the permeable corrosion product layers to the internal zone and remaining Cu-base matrix. The accumulation of chloride ions can be interpreted as an autocatalytic reaction that facilitates the oxidation of copper resulting also in an accumulation of chloride ions and in the formation of cuprite and cuprous chloride, as described in details by Robbiola and co-workers [5]. These considerations show that uncompleted knowledge of corrosion products and degradation mechanisms as well as inappropriate conservation materials and cleaning treatments, could not stop the degradation phenomena and are not able to ensure a long-term chemical-physical stability for the archaeological bronze objects.

In reaching these latter objectives it is fundamental to identify the degradation origin and to correctly select materials and methods able to reliably stop the degradation phenomena, and also to acquire a deep insight into their performances and mechanisms as a function of the chemical composition and metallurgical features of the artefact, as well as of the degradation mechanism.

The results shown above have demonstrated that one degradation source that affect the long-term stability of the Cu-based archaeological artefacts is due to the ubiquitous and nearly constant presence of chlorine inside the corrosion layers that inducesthe cyclic copper corrosion.

The other source of degradation is due to the intrinsic metallurgical features of the archaeological artefacts created during the production of the alloys and the manufacturing of the objects by repeated cycles of cold or hot mechanical work and thermal treatments. These combined treatments induce segregation phenomena along the grain boundaries of the impurities present in ancient and imperfectly refined alloys, thus inducing mechanical weakness and increasing the extent of the inter-granular corrosion phenomena as shown by image B of Fig. 5. Unfortunately, for the first degradation cause, it could be possible to find reliable methods and materials to stop the troublesome role of chlorine, for the second one it is not possible to find a definitive solution but only to propose some precautions.

4 Conclusions

A large number of Cu-based archaeological artefacts found during the excavation of different Mediterranean basin sites have been selected for investigation of their chemical composition, metallurgical features and natural corrosion products (i.e. the patina) to be used for determining the degradation origin.

The results show wide variation of the chemical composition of the alloys that include all kinds of ancient Cu-based alloys such as low and high tin, and also leaded bronzes, copper and copper-iron alloys.

The examination of the alloy matrix shows largely different metallurgical features thus indicating the use of different manufacturing techniques for producing the artefacts. The results of the micro-chemical investigation of the patina show the structures and the chemical composition of the stratified corrosion layers where copper or tin depletion phenomenon are commonly observed with a remarkably surface enrichment of some soil elements such as P, S, Ca, Si, Fe, Al and Cl. This information indicates the strict interaction between soil components and corrosion reactions and products. In particular, the ubiquitous and near constant presence of chlorine in the corrosion layers is observed in the patina of the archaeological Cu-based artefacts found in different contexts in Italy, Turkey, Jordan, Egypt, Spain and Tunisia. This latter occurrence is considered dangerous because it could induce a cyclic corrosion reaction of copper that could disfigure the artefact.

The micro-chemical and micro-structural results also show that another source of degradation of the bronze archaeological artefacts, are their intrinsic metallurgical features whose formation is induced during the manufacturing of the objects, carried out in ancient times by repeated cycles of cold or hot mechanical work and thermal treatments. These combined treatments induce crystallisation and segregation phenomena of the impurities along the grain boundaries and could cause mechanical weakness and increase the extent of the inter-granular corrosion phenomena.

Finally, the results of the large-scale characterisation can help to identify the present conservation state of the archaeological bronze artefacts and can lead to recommendations for selecting tailored conservation methods and materials. These latter should be able to transform, in stable phases, the dangerous copper chlorides or oxy-chlorides, to stop the copper cyclic reaction and to ensure a long life for the bronze archaeological artefacts.

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