Analytical and Practical study of some fighting artifacts from Yemen

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This paper aims to know the effects of microstructure and chemical composition on mechanical properties of Cu-based alloys, to know the effects of weight percentage of tin (and other elements in Cu-Sn diagram/ system) on the material structure and mechanical properties, to know the role of microstructure and chemical composition in deterioration process and to identify the types of corrosion products of selected objects as well as their constituting metals in order to carry out scientific treatment and conservation to avoid the further deterioration.

Over centuries, foundry workers tried, mostly by trials and errors, to determine the most favourable amount of tin, according to the kind of artifact and its using, also they used to improve the quality of their productions [1]. Ancient bronze consisted of tin that ranged from about 2% to about 16%, it has been known since ancient times that tin increases the strength of copper and that lead improves fluidity of the cast. However, it should be noted that apart from the generally recognized and widely accepted Cu-Sn diagram/system that allows to link the weight percentage of tin with different phase structures and corresponding strength and elongation to rupture for tin bronzes, the influence of additional alloying elements such as iron (Fe), nickel (Ni), antimony (Sb), silver (Ag), bismuth (Bi), zinc (Zn), phosphorus (P) and sulphur (S) on the final quality of artifact materials and their effects on the mechanical properties including failure and fracture of tin bronzes has only scarcely been studied and rarely reported. There are a lot of studies on ancient and historical bronzes have tried to establish the chemical characteristics and structure of natural patinas grown on artifacts exposed for long periods of time to soil atmosphere, water or sea water, the long term corrosion of bronzes is accompanied by structural transformations leading to a steady state. Different surface patterns have then been observed, depending on the corrosive environment (chemical composition, pH, resistivity, etc.) but also on other non-negligible parameters such as historical periods, metallurgical techniques or even kind and size of the artifact (monuments, large sized statues, smaller objects). Furthermore most of the published studies have also been carried out in view of improving conservation methods in order to prevent the so-called bronze disease, a post burial cyclic corrosion phenomenon occurring in the atmosphere, due to the presence of cuprous chloride within the patinas rather than to get a deeper insight into the corrosion behavior of Cu-Sn alloys in natural environments [2-14].

This study aims to know the effects of microstructure and chemical composition on mechanical properties of tin bronzes were studied from different types of fighting artifacts materials produced in Yemen in ancient days, to know the effects of weight percentage of tin (and other elements in Cu-Sn diagram/ system) on the material structure and mechanical properties, to know the role of microstructure and chemical composition in deterioration process and to identify the types of corrosion products of selected objects as well as their constituting metals in order to carry out scientific treatment and conservation to avoid the further deterioration.

To achieve that multivariate analysis were performed on some selected artifacts by means of the combined use of metallographic microscope, scanning electron microscopy combined with energy dispersive spectrometry (SEM&EDS), X-ray diffraction (XRD) techniques.

MATERIALS AND METHODS

DESCRIPTION AND CONDITIONS

The investigations were conducted on four front parts of spears; they were discovered by the Yemeni mission in El-Shab El-Aswad site, Jahran, Yemen, season 2006. They date back to Qatabanian period in Yemen (1500 B.C) and they can classify as the following:

- The spear a, is separated into two parts, the completely length of the spread is 26 cm (the length of hand 16.5 cm with thickness 0.5 cm, the length of the head is 11.5 cm, the maximum width of the head is 1.7 cm and the minimum 0.5 cm). It suffered from deterioration factors, covered with a thick layer of black corrosion products mixed with soil dirt's (Figs. no1a, 2).
- The spear b, the completely length of it is 19 cm (the

Figs. 1, 2 - Shows the spears before the treatment.

length of hand 15 cm, the length of the head is 4 cm, the maximum width of the head is 0.7 cm). It suffered from deterioration factors, covered with a thick layer of black corrosion products mixed with soil dirt's (Figs. no.1b).

- The spear c, the completely length of the spread is 14.5 cm (the length of hand 12 cm with thickness 0.5 cm, the length of the head is 2.5 cm). It suffered from deterioration factors, covered with a thick layer of black corrosion products mixed with soil dirt's (Figs. no.1 c).
- Ahead of spear d, the completely length of the spread is 9.5 cm (the length of hand 2.5 cm, the length of the head is 7 cm, the maximum width of the head is 1.5 cm), it has a geometric decorations in the middle. It suffered from deterioration factors and covered with a layer of black corrosion products (Figs. no.1d).

Physio-chemical Characterization

The physical and chemical characterization of the objects was performed by metallographic microscope (ME), scanning electron microscope & energy dispersive spectrometry (SEM&EDS) and x-ray diffraction (XRD). ME was used to show the microstructure of the metal and aspects of deterioration which spread on the metal surface, SEM&EDS was used to more actually examination for the spears and to determine the chemical composition of the spears and X-Ray Diffraction analysis was used to investigate the corrosion products, it can provide valuable information related to the burial condition of the spears as well as the composition of the metal or the alloy.

Metallographic Microscope Examination (ME)

Metallographic examination for samples of the spears were performed to show the microstructure of metal and aspects of deterioration which dispersed on the metal surface. It allows a great deal of information to be obtained about the quality of the material used for manufacturing as well as information related to the technology of fabrication [15]. Unfortunately accessing this information normally requires an invasive intervention on the artifact: a small fragments need to be detached from the spears and mounted as a cross section by an embedding procedure, then they were polished using silicon carbide papers of 400, 600, 800 and 1200 grit. The polished samples were washed with distilled water, degreased with ethanol. Ferric chloride aqueous solution was used as etching reagent for metallography; the samples were mopped dry with soft clean cloth followed by observation under a metallographic microscope (Figs. no. 3- 6).

Scanning Electron Microscope Examination and Energy Dispersive Spectrometry (SEM&EDS)

Four small samples were taken from the spears and examined by SEM&EDS to show the microstructure, the appearance of deterioration spots and the chemical composition of the spears, by using an Inspect S50 (FEI), image size: 1000 x1000, HV: 20.0kV.
The obtained examination photos are given in (Figs. 7-10), Scans and the identified elements are given in (Figs.11-14 and Table 1).

X-Ray Diffraction Analysis (XRD)

X-Ray diffraction analysis was carried out for corrosion product. Four samples represent all the corrosion products on the surface of the spears were taken and analyzed by using a Philips X-Ray, Diffract meter type: pw1840 with Cu k& Radiation.
The aim of this analysis is identification the corrosion compounds in order to decide whether it is authentic, stable and suited to certain kinds of conservation treatment. This information can assist in choosing the best environment for the selected spears in storage or in show-cases. The obtained diffraction scan given in (Figs. no.15-18) and the identified compounds represented in the (table 2).

Fig. 3 - ME ex., for a sample from the spear a, shows crevice corrosion dispersed in the alloy.

Fig. 4 - ME ex., for a sample from the spear b, shows the micro cracks disturbing of the surface.

Fig. 5 - ME ex., for a sample from the spear c, shows the pitting corrosion.

Fig.6 - ME ex., for a sample from the spear d, shows the crevice corrosion dispersed in the alloy.

Treatment and conservation of the spears

According to the obtained examination results the spears have a good metallic state, but they are covered with thick layers of corrosion products, chemical treatment was chosen assisted by skilled mechanical cleaning, this helped us to reveal and discover the original surface topography.
After searching in the previous studies [16,17] and a serial of tests were carried out to determine which chemical compounds would be effective without damage the objects the least by varying the concentration and time of contact, it was found that solution of Sodium Hexametaphosphate, Calgon, is the least damaging and fastest acting solutions. It is recommended as being safe for removing calcareous deposits, cupric oxide and cuprous oxide.

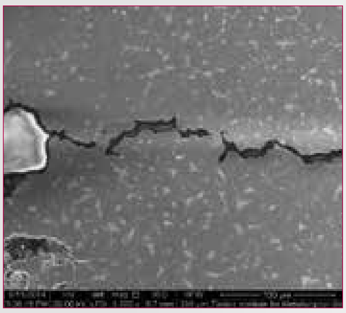

Fig. 7 - SEM ex., for the spear a, shows the stress corrosion and cracks(1000x).

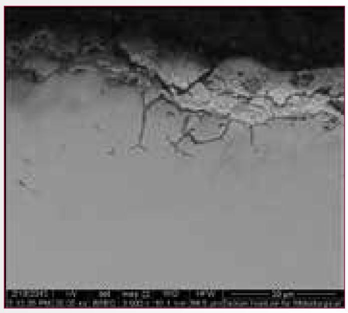

Fig. 8 - SEM ex., for the spear b, shows cracks and distorting of the edge of the alloy (3000x).

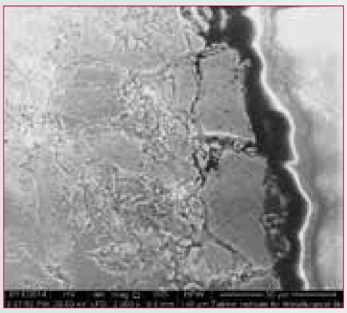

Fig. 9 - SEM ex., for the spear c, shows the cracks and distorting the surface (2000x).

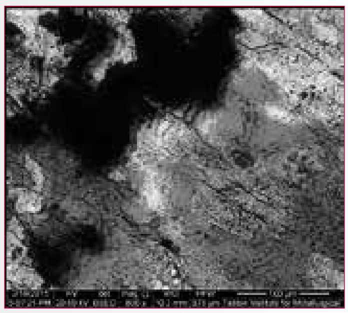

Fig. 10 - SEM ex., for the spear d, shows the pitting corrosion and distorting the edge(800x).

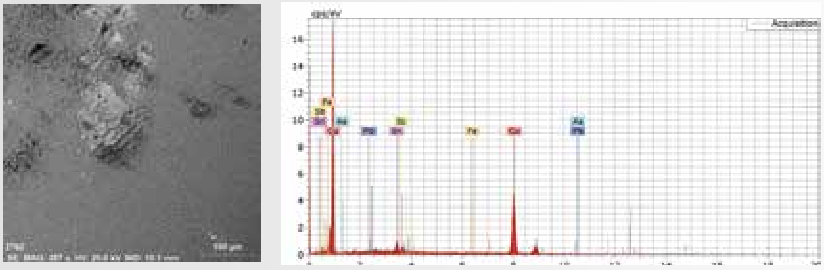

Fig. 11 - Shows SEM&EDS ex., of the spear a, the photo shows consist of the alloy, tin appears in a light color, pitting corrosion and SEM&EDS Scan shows the elemental composition of the spear a.

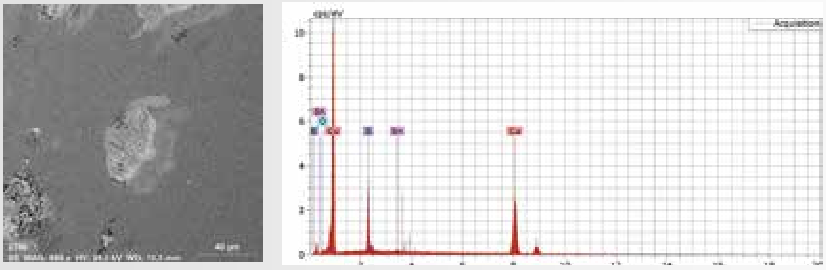

Fig. 12 - Shows SEM&EDS ex., of the spear b, the photo shows the spots of sulfate appears in a white color and SEM&EDS Scan shows the elemental composition of the spear b.

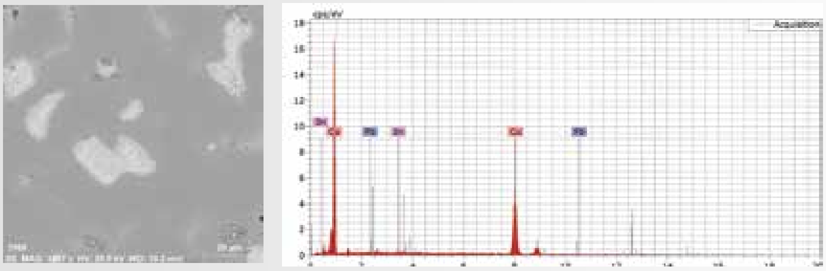

Fig. 13 - Shows SEM&EDS ex., of the spear c, the photo shows consist of the alloy, pitting corrosion dispersed in the alloy and SEM&EDS Scan shows the elemental composition of the spear c.

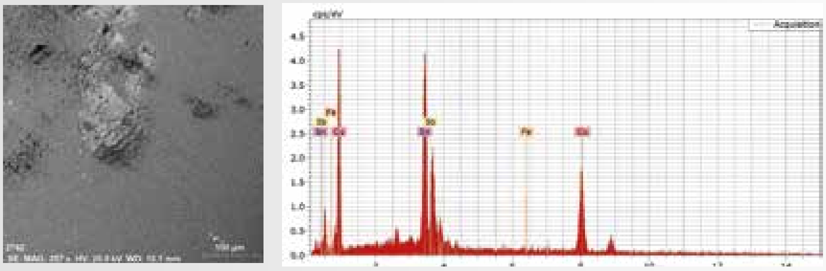

Fig. 14 - Shows SEM&EDS ex., of the spear d, the photo shows the consist of the alloy, tin appears in a white color, pitting corrosion and SEM&EDS Scan shows the elemental composition of the spear d.

The treatment procedures included the following steps:

- Soaking the spears completely in dilute solution of Calgon [Sodium Hexametaphosphate $Na(PO_3)n$], that was changed many times assisted by gentle mechanical cleaning with silk brush from time to time to dissolve the corrosion layers and the calcareous sediments. This step succeeded in removing the calcareous sediments, cupric oxide and cuprous oxide.
- After that the spears were soaked in water and washed by a tooth brush to dislodge residue from crevices.
- Repeated washing in hot deionized water baths with altering heating and cooling to ensure flushing capillaries to remove any chemical residues.
- Drying in repeated baths of ether and ethanol followed by drying in hot saw dust and mopped dry with soft, clean cloth.
- Finally the spears were isolated with paraloid B-72 dissolved in Acetone 3% by using a brush (Figs. no.19, 20).

RESULTS AND DISCUSSION

Metallographic examination of the spears indicated a non-homogenous structure, localized corrosion spots dispersed on the metal surface represent in pitting corrosion and disbursing the surface of spear a, crevice corrosion dispersed in the alloy of spear b, pitting corrosion in the spear c and crevice corrosion in the spear d. In addition to the elongation of the bronze grains revealed the use of the hammering method after casting to manufacture the spears, this played a negative role in their deterioration due to the existed strains inside the metallic structure (Figs.3-6).
SEM examination showed the microstructure, the content of the alloy and corrosion aspects of the spears, Tin appears in a whited areas disperse in the alloy of spears a and d (Figs.7, 10, 11, 14), sulphide and Oxygen appear in a white spots in the alloy of spear b (Fig.12), the corrosion aspects such as pitting corrosion, stress corrosion, crevice corrosion and micro cracks dispersed in the alloy. All of these corrosion aspects disbursed the surfaces of the objects (Fig.7- 14); SEM examination confirms metallographic examination results.
SEM&EDS investigation results indicated that the majority of the investigated spears were made of Tin bronze; all spears had a large content of copper and one of the alloying metals such as tin, with some traces from Oxygen and Sulphide. Tin content varied from about 1.24% to 57.04%, the presence of tin could be likely enhanced via cycles of oxidation and selective copper corrosion processes, thus resulting in a tin surface enrichment as a semi-transparent amorphous-like tin oxide (Sn2O) film, as well as a copper depletion at the outer surfaces [18-19]. Furthermore the bulk alloy structure of these bronze spears clearly indicates a non-homogeneous that can be preferentially attacked by aggressive agents. Tin bronze for the selected objects were Cu/Sn alloy, with the tin content ranging from as low as 1.24% in the spear c, 1.68% in the spear b, 8.44% in the spear a and as high in the spear d about 57.04%. The structure was therefore created by the alpha phase in spears a, b, c influenced by

Elements Samples	Cu%	Sn%	Pb%	Fe%	O%	S%	Sb%	Total%
Spear a	91.50	8.44	00.0	0.06	00.0	00.0	00.0	100.00
Spear b	80.54	1.68	00.0	00.0	1.85	15.92	00.0	100.00
Spear c	98.21	1.24	0.55	00.0	00.0	00.0	00.0	100.00
Spear d	42.17	57.04	00.0	0.19	00.0	00.0	0.60	100.00

Table 1 shows SEM&EDS analysis results of the spears

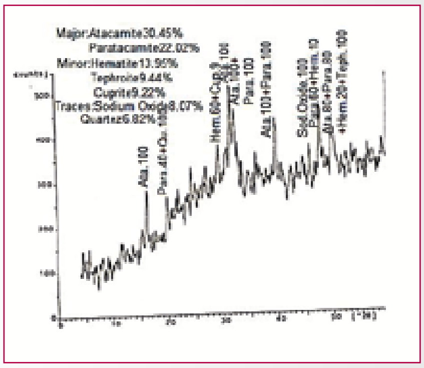

Fig. 15 - Shows XRD scan for the corrosion products of the spear a.

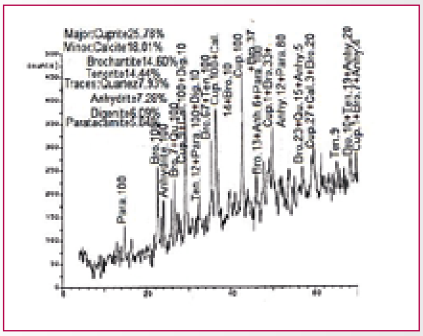

Fig. 16 - Shows XRD scan for the corrosion products of the spear b.

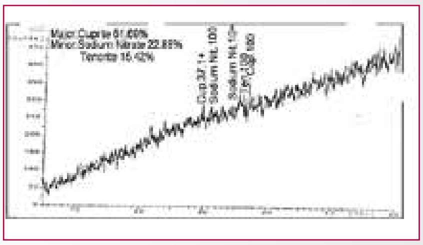

Fig. 17 - Shows XRD scan for the corrosion products of the spear c.

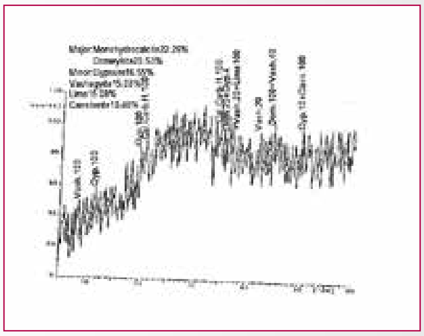

Fig. 18 - Shows XRD scan for the corrosion products of the spear d.

Fig. 19 - Shows the spears after treatment and conservation .

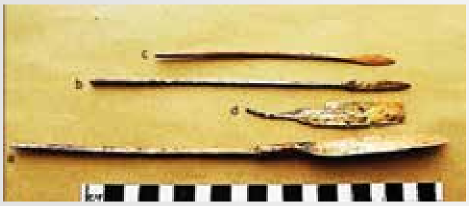

Fig. 20 - Shows the second side of the spears after treatment and conservation.

tin about 57.04%, the structure was therefore created by the delta phase, so the alloy was a non-homogenous and has bad mechanical properties including brittleness, failure and fracture of tin bronze. The influence of alloying and harmful elements on the mechanical properties and qualitative are shown in (Figs. no 3-10).

Analytical investigations revealed that the main corroding agent is represented by chlorine containing species that induce the formation of dangerous copper chlorides and Oxy-chlorides at the interface between the metal surface and the outer most corrosion products layers via a continuously occurring reaction (Figs.15-18 & Table 2). For many archaeological objects the reactive cuprous chloride (CuCl) species is considered as the principal agent of the so called bronze disease, the process of interaction of chloride- containing species within the bronze "Patina" with moisture and air, often accompanied by corrosion of the copper alloy itself [20-21].

X-Ray diffraction analysis of the corrosion products of spears (Figs.15-18 and Table 2), revealed the presence of different minerals including Atacamite(Cu2(OH)3Cl), Paratacamite(Cu2(OH)3Cl), Cuprite (Cu2O), Monohydrocalcite (CaCO3.H2O), Domeykite (AsCu3), a minor compounds of Cassiterite (SnO2), Sodium Nitrate(NaNO3), Tenorite (CuO), Calcite (CaCO3), Lime CaO, Brochantite (CuSO4.3Cu(OH)2), Gypsum (CaSO4.2H2O), Tephroite (Mn2SiO4), Hematite (H2O3), Vashegyite (Al2(PO4)3 (OH)3.xH2O) and traces from Sodium Oxide (Na2O), Quartz (SiO2), Anhydrite (CaSO4), Digenite(Cu9S5). Naturally, the corrosion products are dependent on water-soluble salts in the soil, inversely, the surrounding soil has been enriched in copper and other metals

Major	Minor		Traces		
The spear a	Atacamite($Cu_2(OH)_3Cl$) Paratacamite($Cu_2(OH)_3Cl$)		Hematite (H_2O_3) Tephroite (Mn_2SiO_4) Cuprite (Cu_2O)		Sodium Oxide (Na_2O) Quartz (SiO_2)
The spear b	Cuprite (Cu_2O)		Calcite ($CaCO_3$) Brochantite ($CuSO_4.3Cu(OH)_2$) Tenorite (Cu O)		Quartz (SiO_2) Anhydrite ($CaSO_4$) Digenite(Cu_9S_5) paratacamite($Cu_2(OH)_3Cl$)
The spear c	Cuprite (Cu_2O)		Sodium Nitrate($NaNO_3$) Tenorite (Cu O)		-------
The spear d	Monohydrocalcite ($CaCO_3.H_2O$) Domeykite($AsCu_3$)		Gypsum ($CaSO_4.2H_2O$) Vashegyite ($Al_2(PO_4)_3(OH)_3.xH_2O$) Lime (CaO) Cassiterite (SnO_2)		-------

Table 2 shows XRD analysis results of corrosion products of the spears.

from the degrading object. As shown in Table 2, cuprite was dominating among the corrosion products. The presence of Cuprite (Cu_2O) is due to selective corrosion of the main alloying element, which is re-deposited after dissolution onto the surface of the objects, thus forming a copper enriched layer.

The presence of basic copper chloride is related to the sandy and saline nature of the soil, whereas the spears were buried. It played an important role in their severe corrosion, this soil which is porous and changed from Sub-saturation to saturation with water, had different salt ions, specially the dangerous chlorine ion; this circulation of saline water in the soil had a serious effect on the objects.

The most frequent copper hydroxide salt was Atacamite, formed through reaction between the spears and Chlorine Ion in the soil. The cuprous chloride "CuCl" cyclically reacts with Oxygen and atmosphere water "humidity", thus giving rise to formation of 2(Cu_2 (OH) 3Cl), Atacamite and its polymorphs. These Oxy-chloride compounds react with copper to form cuprous chloride and water, and in this way Cu, Cl, O_2 and H_2O are converted in Cuprite Cu_2O and Atacamite in a cyclical and continuous process [20-21]. The final products of the reactions are light green powdery, voluminous basic chlorides of copper, which disrupt the surface and many disfigure the artifacts. Also, the nature and composition of the soil from the excavation site is of great importance for the degradation of the archaeological artifacts, but in the case of metal bronze objects, humidity and chlorides are the key factors. In order to stop the above reported cyclic reaction and to ensure a long life for the bronze artifacts, suitable materials and methods to transform copper chlorides in stable and inert phases are required.

The presence of Brochantite ($CuSO_4$.3Cu (OH) 2), Anhydrite ($CaSO_4$) and Digenite (Cu_9S_5) in corrosion products of the spear b (Fig. 16 &Table 2) reflected the chemical composition of the spear b, which has a high amount of Sulphide reaches to 15.92% as it shown in SEM&EDS analysis results (Fig. 12&Table 1), it indicated that there is a strong relation between the chemical composition of the alloy and the kind of corrosion products. The sulphide corrosion has, however been produced while the selected objects has been in the care of Dhamar museum, Yemen. Many authors have studied the form of sulphide formation on bronze which occur in museums and the reaction between copper and hydrogen sulphide [22-28], in most cases it is described as resulting in an even layer. Sulphide may be come from the industrial pollution, an unfortunate choice of showcase materials or the presence of Carbon Sulphide which, as pointed out recently, is quite wide spread and in comparatively large quantities, finally Sulphide may become from the first step of extraction copper from its ores.

The presence of Calcite ($CaCO_3$), Lime (Ca O) and Monohydrocalcite ($CaCO_3.H_2O$) in the XRD analysis results of spears b and d (Fig.16, 18 &Table 2) corrosion products is most probably formed by the reaction of soluble calcium bicarbonate with hydroxide ions produced in the Cathodic reaction of Oxygen, indicated that the soil usually has high Carbon dioxide contents and may be chemically very aggressive because the Carbon dioxide may react with water to form Carbonic acid, which may attack metals directly and prevent the formation of a protective film surface. A calcareous soil may also act in a quite benign, however, especially if Carbon dioxide and water produce the soluble Calcium bicarbonate. This may act to protect the objects from corrosion, since Calcium bicarbonate is a salt of a weak acid, its aqueous solution is very alkaline and by binding with Carbon dioxide, it prevents the extensive dissolution of Copper (1) ions. At values of pH ›8Calcium Carbonate precipitates as Carbonate, and in subsequent acidic condition, this may dissolve instead of Copper (11) compound, the overall PH in dilute natural ground water is principally controlled by this $CaCO_3$-H_2O-Co2 equilibrium.

The presence of Tin Oxide in (SEM-EDX, Fig. no. 14 &XRD, Fig. no. 18) reflected the chemical composition of the spear d. and indicated that there is a strong relation between the chemical composition of the alloy and the kind of corrosion products. The existence of Sodium Oxide Na_2O in corrosion products analysis results of spear a, and Sodium Nitrate ($NaNO_3$) in spear c (Figs. 15, 17 & Table no. 2) indicated that the burial environment was rich with sodium salts. Also the existence of Hematite Fe_2O_3 in a minor amounts in corrosion products of the spear a, (Fig.15 and Table 2), may be as a result of migration of Iron corrosion from adjacent iron objects to the selected bronze spears in the burial environment or from the buried environment itself as it is very rich with Iron compounds, this indicates the strong interaction between soil components and corrosion products.

CONCLUSION

- The combined used of ME, SEM-EDS and XRD analytical techniques have provided good insight into the bulk nature and surface corrosion products grown on the objects during the archaeological burial.
- The spears are made of a binary alloy, composed of copper and tin. The Sn content lies between (8.44% in spear a, 1.68% in spear b, 1.24% in spear c and 57.04% in spear d).
- The study indicates that soil conditions allowing access for air and water to the object at the same time increases the corrosively, because the soil where the spears were found is a sandy soil, conditions will be especially corrosive for metals in soil within an area just above the ground water table (where the soil pores are partly filled with water). The extension of the corrosive soil zone will depend on the grain size distribution among the soil particles, which affects the capillary rise of the ground water and also the hydraulic flow through the soil.
- The formation of copper sulphide on bronze objects is caused by the presence of sulphur compounds in the surrounding air or from the first processes of extracting the copper (spears based material) from its ores.
- To stop the cyclic reaction of corrosion process and to ensure a long life for the bronze artifacts, suitable materials and methods to transform copper chlorides in stable and inert phases are required.

Abstract

This paper aims to know the effects of microstructure and chemical composition on mechanical properties of Cu-based alloys, to know the effects of weight percentage of tin (and other elements in Cu-Sn diagram/ system) on the material structure and mechanical properties, to know the role of microstructure and chemical composition in deterioration process and to identify the types of corrosion products of selected objects as well as their constituting metals in order to carry out scientific treatment and conservation to avoid the further deterioration. The chemical composition analysis declared that the artifacts are made of bronze alloy. The patina of the examined artifacts were consisted of two layers and composed of Cuprite, Atacamite, Paratacamite, Tenorite and Quartz. Metallographic microscopy, Scanning electron microscopy with energy dispersive spectrometry (SEM&EDS) and X-ray diffraction were used to describe the main properties of patina layers and identified the chemical composition. The results were interpreted and classified according to chemical composition of the artifacts. Finally the obtained results helped us in treatment and conservation the selected objects.

Keywords

Cu-based alloys; long-term Corrosion; Multivariate Analysis; Microstructure; Chemical composition; Conservation

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