INTERNATIONAL JOURNAL
OF
CONSERVATION SCIENCE

ISSN: 2067-533X Volume 9, Issue 2, April-June 2018: 277-290 www.ijcs.uaic.ro

AN INVESTIGATION OF THE CORROSION BEHAVIOR OF SOME IRON ARTIFACTS BELONGING TO THE EARLY IRON AGE

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Abstract

The corrosion process of two iron dagger handles decorated with bronze strips found from the Ziviyeh area, which is one of the important Iron Age sites in the northwest of Iran, is thoroughly investigated. X-ray radiography was used to obtain the damages and corrosion zones of the artifact. Optical and scanning electron microscopies were used to study the microstructure of cross sections and to achieve structural details about the metal matrix and corrosion layers. The X-ray diffraction method was used to study the chemical characterization of corrosion products. The results of studies have shown that severe stress on bronze strips is caused by the formation of goethite and lepidocrocite compounds and their increased volume. Stress corrosion along the inter granules and cracking in some of the bronze strips are observed. The created cracks in the magnetite layers provided shortcuts to transfer the moisture and corrosive anions. The atmospheric corrosion of the remaining ferrous parts continued actively by dewatering corrosion products and creating wet blisters and holes filled with oxyhydroxide products. The formation of oxide compounds of copper and tin on the surface of bronze strips followed a slow process of uniform corrosion in bronze strips to a limited extent.

***Keywords**: Corrosion; Iron–bronze bimetallic artifacts; Early Iron Age; Iran; Ziviyeh*

Introduction

The corrosion of copper and bronze artifacts is being studied for many years. Since 1826, when a helmet was found in the sea and red oxide products of cuprite and copper were identified as a result of the process of redeposition of copper [1], the corrosion behavior on the historical artifacts has been studied by many scientists. The formation of the cuprite and its effect on the continuation of the corrosion behavior have been addressed in various studies [2-5]. In addition, the patina of ancient bronze can also indicate different forms of tin-rich corrosion layers depending on environmental conditions [6, 7]. Similar studies have been conducted on Iranian bronze artifacts. The obtained results about the dissolution process and the extraction of copper during the decuprification process are examples of these studies on ancient bronze objects belonging to Haft Tappeh historic site, Khuzestan, Iran [8]. In addition, due to the formation of the galvanic cell, copper is protected in contact with the more active metals, including iron, and this process can be predicted in the iron–bronze bimetallic artifacts. The construction of iron–bronze bimetallic artifacts at the beginning of the Iron Age in the north, northwest, north-central, and central Zagros regions, Iran, is one of the techniques used in the manufacture of metal artifacts [9]. The examples of iron artifacts from Central Zagros of Iran

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include valuable iron artifacts decorated with bronze pieces, such as one of the largest group of Lorestan battle axes with decorations in the form of animals [10, 11].

The ability of artisans in the northwest of Iran, such as Hasanlu site, to use sponge iron in fabricating artifacts and decorating them with bronze parts resulted in valuable works such as pins in the form of sleeping lion [12]. In many cases, due to the high corrosion rate of iron a few remnants of these bimetallic artifacts exist today. Iron corrosion has an electrochemical nature and it occurs in the presence of an aqueous phase on the metal surface [13]. In the iron corrosion reaction taking place underground, an anodic reaction occurs on the surface of the metal, and Fe^{2+} ions directly react with the hydroxide ions (HO^-) and eventually oxidize and hydrolyze to produce iron oxyhydroxides. Of course, the reaction of metal oxidation and the formation of metal oxides and their conversion to other corrosion products are possible after excavation and exit of the object from the ground [14]. The conversion of these compounds to stable iron oxide is also very likely to occur. However, the holes and open surfaces in the corrosion layer of ancient iron are filled with acidic Fe(II) chloride in the process of the corrosion of cracks [15].

The result of the corrosion process is to increase the acidity and concentration of chloride [16, 17]. Corrosion accelerates with increasing relative humidity in spite of Fe(II) chloride tetrahydrate and *akaganeite* [18]. Generally, iron corrosion processes occur under anodic conditions in most of the buried iron objects. The corrosion layer is more fragmented in anodic controlled processes, for example, in the presence of chloride ions [19]. In addition to the usual corrosion of iron, the acceleration of galvanic corrosion process at the connection site of iron to copper is encountered in bimetallic artifacts. Limited technical studies have been conducted on iron artifacts, especially on the bimetallic artifacts of the early Iron Age in Iran. *Reed Knox et al.* (1963) conducted microstructure studies on Hassanlu iron swords that had a microstructure in the form of pseudomorphic pearlite colonies in an iron oxide matrix [20]. An example of studies on the early Iron Age artifacts of Iran includes Lorestan iron swords that had varying carbon contents [21]. There is a little information about iron–bronze bimetallic artifacts that are discovered from excavations carried out in Iran’s Iron Age sites. As the numbers of these kinds of artifacts are low and they are unique because of the used techniques to make them, it is hard to access these artifacts for further analysis. Hence, this study investigates the corrosion process of discovered early Iron Age bimetallic artifacts, with access to samples from the Ziviyeh site as one of the important Iron Age sites in Iran.

Experimental

Many iron artifacts have been discovered in excavations in Ziviyeh and Changbar. Some of them, dated to Iron Age II [22-23]. Ziviyeh is an ancient site situated at a distance of 45 km from the Saqqez city in Kurdistan Province in the northwest of Iran. Ziviyeh is essentially well known for numerous archaeological studies conducted on various remarkable objects found in this area in the 1940s. Short-term field studies on surface surveys and some limited excavations in Ziviyeh were conducted in the 1960s by Robert Dyson (1963–1965). The extensive archaeological excavations in Ziviyeh and Changbar were started in 1976 under the supervision of Nusratollah Motamedi. After being suspended for several years, it was first supervised by Motamedi and subsequently by Simin Lakpur in 1994 [23]. In order to examine the corrosion, in this study, two artifacts with a relatively similar appearance were selected from the Ziviyeh site, including a residue of hollow objects in the form of dagger handle with bronze tapes (Fig. 1).

X-ray radiography (Rigaku’s Radioflex–100CSB model) was used to investigate the artifacts and ensure the presence of remaining metal core. A section of the artifact was cut at the interface of the decorative type to the main body to conduct cross-sectional microscopic studies on the selected artifacts. Surface deposits and corrosion products were sampled separately. An

X-Ray Diffraction system (X'Pert PRO MPD, PANalytical Company, the Netherlands) was used to investigate the corrosion products. Leika/Wild M8 Stereo Microscope was used to investigate the morphology of the surface of the metal samples. After mounting the selected samples in epoxy resins and using various emeries (100–2000 mesh silicon carbide sheets), the sample preparation steps were completed to study the polished metal surfaces and oxidized layers. The final polishing was performed using polishing felt and diamond suspension. An Olympus PMG3 reflected light microscope was used to study the polished surface of the samples. In order to obtain images of various phases of the microstructure of the samples and analyze them for the elemental distribution, TESCAN scanning electron microscope (SEM), VEGA model, with an EDX device was used.

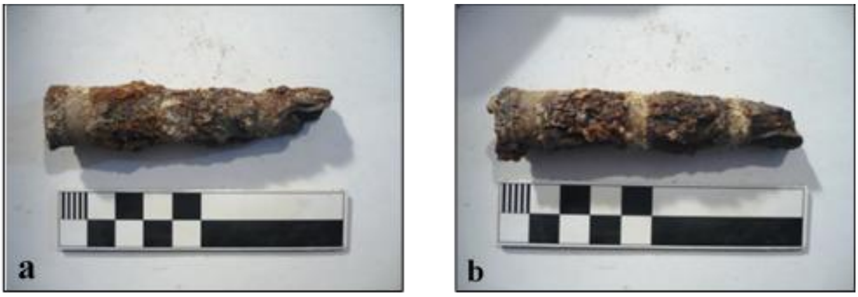

Fig. 1. The selected Iron-Bronze Bimetallic Artifacts from Ziviyeh:
a) Ziviyeh artifact–1; b) Ziviyeh artifact–2

Results and Discussion

The preliminary chemical analysis revealed that the body of the above-mentioned artifact is made of iron alloys and decorated with decorative strips of copper and tin alloys.

The impurity phases with a preferential orientation were observed in the iron substrate as the key material used in the main body of the dagger handle (Figure 2a). In the case of Ziviyeh artifact–1, the tin bronze alloy (8.37% Sn) was used as decorative tapes. In the case of Ziviyeh artifact–2, with a relatively similar trend, the tin bronze (10.06% Sn) with lead metal inclusions (0.22% Pb) was uniformly distributed in the metal matrix as decorative tapes.

The microscopic images show the uniform distribution of gas holes in the metal matrix of the copper phase prior to etching operation (Fig. 2b), confirming the application of casting technology in copper decorative tapes on the body of these artifacts. In addition, in parts of the body of one of these pieces, the iron connection is not fully completed, which is the evidence of bronze flow and freezing (Fig. 2c).

In Figure 3, X-ray radiography shows that metal cores, besides oxide layers, are still present in some parts of the iron body despite the corrosion in these artifacts. However, the used metal has a completely different condition for decorative tapes, except in some parts where traces of cracks are observed it is almost intact (Fig. 3).

In the radiographic image, no connection areas have been observed, but the cracks are longitudinal and along the same line, which suggests the possibility of a connection in this area.

According to the X-ray diffraction (XRD), the results of the analysis of corrosion products are evidence of the formation of oxyhydroxide compounds, such as *lepidocrocite* (γ-FeOOH) and *goethite* (α-FeOOH) on the surface of the main body in both samples (Fig. 4).

The mechanisms of the corrosion behavior of metal artifacts depend on the chemical, mechanical, and morphological characteristics of the Fe(II)-based layer that develops between the metal surface and the environment. Primarily, Fe(II) compounds, such as hydroxychloride $\beta\text{-}Fe_2(OH)_3Cl$, *chukanovite* $Fe_2(OH)_2CO_3$, or *siderite* $FeCO_3$, are considered as the corrosion products of historical iron objects in anoxic environments [24]. However, generally, oxides and oxyhydroxides are the major corrosion products that form on the surface of ironworks in the presence of oxygen. The results of the chemical analysis of corrosion products indicate that the corrosion of the two dagger handles of the historic site of Ziviyeh occurred in the presence of oxygen.

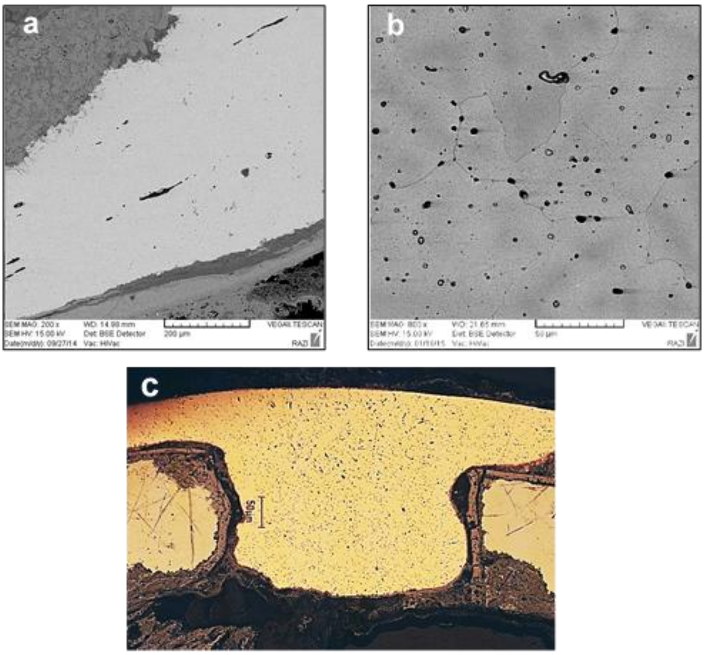

Fig. 2. Scanning electron microscopic (SEM) and optical microscope images (OM):
a) SEM from Iron matrix and impurities. b) SEM from bronze matrix of the strips.
c) OM(12.5X) from bronze layer of the Ziviyeh artifact–1

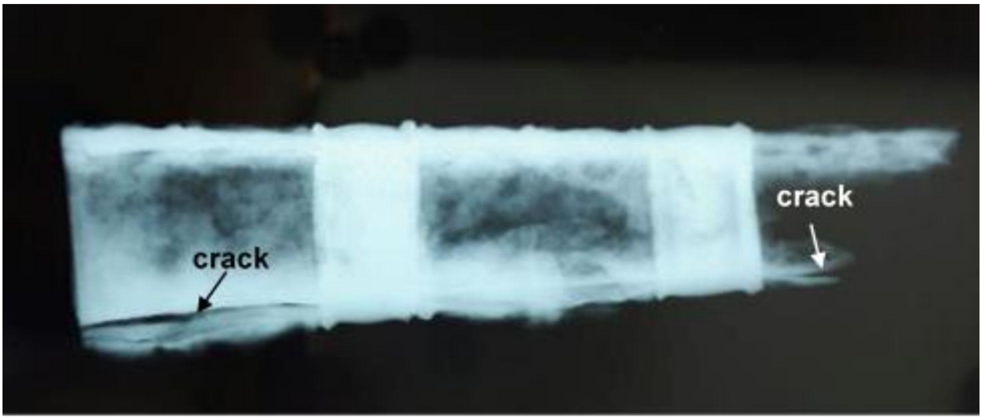

Fig. 3. X-ray image of part of Ziviyeh artifact–2

According to XRD results, the secondary green and blue products of copper carbonates that have been identified with the wet chemical analysis are produced by the sequestration of white calcite compounds ($CaCO_3$) on the surface of both compounds, especially on bronze tapes. In the Ziviyeh artifact–2 sample, most of the corrosion products are oxide products and iron oxyhydroxides. Moreover, these products are also observed on the copper tapes. The content of copper and tin products is much lower than that of iron corrosion products (Fig. 5)

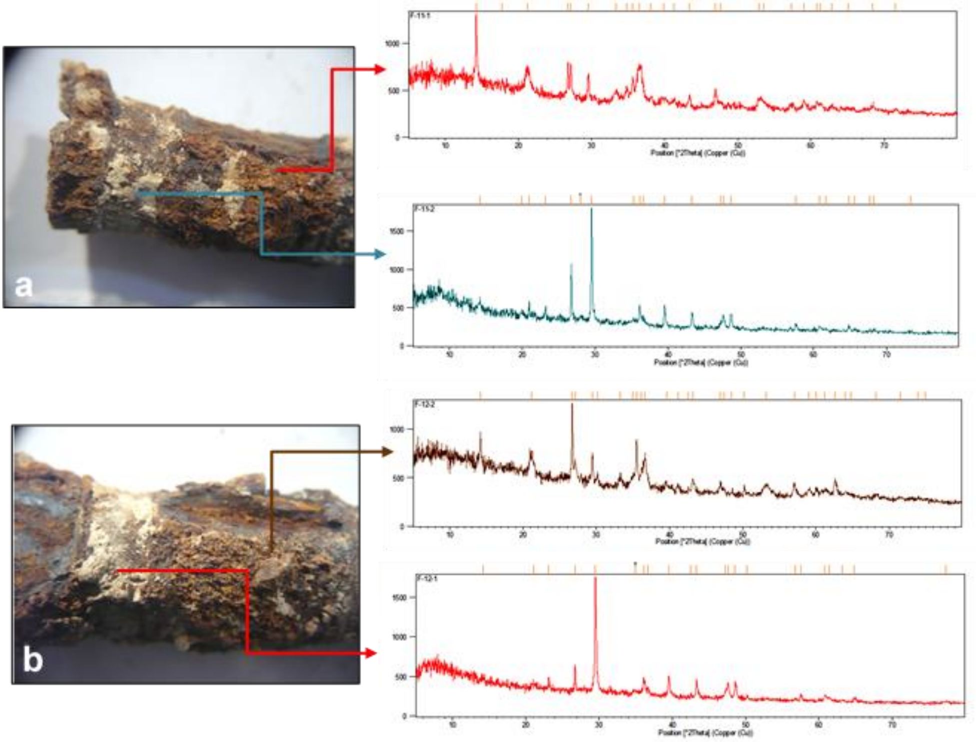

Fig. 4. Stereomicroscopic images (6X) of iron corrosion products and sequestered compounds on bronze and XRD spectra of corrosion products and surface sediments: a) Ziviyeh artifact–1; b) Ziviyeh artifact–2

Fig. 5. Polarized light microscope image (12.5X) of layers on the cross section of Ziviyeh artifact–2

The formation of the major products of iron corrosion and their distribution even on the surface of bronze tapes is confirmed by the results of the analysis of elemental distribution as shown in Figure 6. Moreover, iron oxides and oxyhydroxides were observed to be the major layers of corrosion products. Furthermore, corrosion exacerbation at the interface of two alloys is caused by the galvanic joint between iron and bronze, and the development of corrosion in the iron part is also observed (Fig. 6).

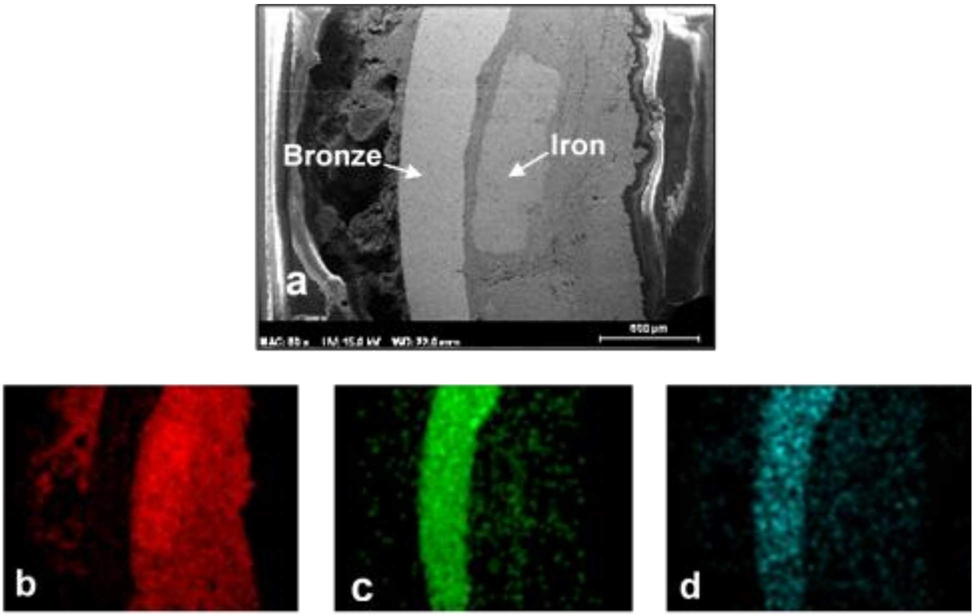

Fig. 6. SEM image and distribution map in cross-section:
a) SEM image as backscatter of Ziviyeh artifact–2 cross-section;
b) Distribution map of Iron; c) Distribution map of copper; d) Distribution map of tin

In addition, the optical microscopic image without etching operation shows intergranular corrosion in the iron structure for Ziviyeh artifact–2, indicating the formation of the ferrite-pearlite microstructure in the body of the artifact. The corrosion is initiated from grain boundaries and grows as intergranular corrosion (Fig. 7).

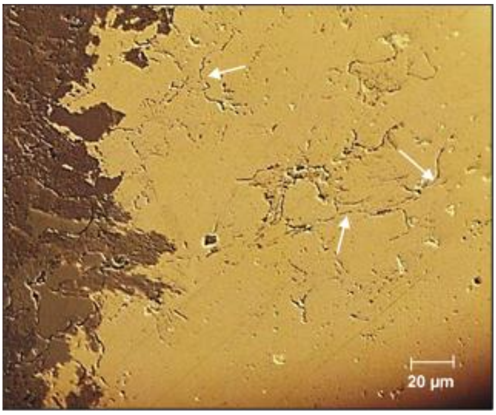

Fig.7. An Optical microscope image of intergranular corrosion
in the iron structure of Ziviyeh artifact

Because of chemical, structural, and phase heterogeneity, the grain boundaries are considered the heterogenic area, which is the main reason of intergranular corrosion in iron alloys [25].

The formation of iron oxides or oxyhydroxides between the magnetite layers and a thin layer of copper and tin oxide products on the inner and outer surfaces of the bronze tape adjacent to the iron is confirmed by the general structure of the metal matrix and corrosion layers in the electron microscopic image (Fig. 8) and the results of elemental analysis (Table 1).

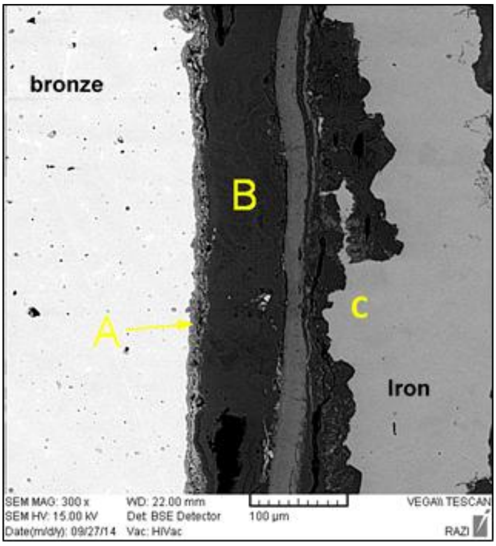

Fig. 8. SEM image of layers on the cross section of Ziviyeh artifact–2

Table 1. EDX elemental analysis of corrosion layers in Figure 8 related to Ziviyeh artifact–2.

Phase	Fe	Cu	Sn	O	Si	Mg	Al
A	31.99	23.27	8.78	29.66	2.74	1.44	2.11
B	66.01	2.05	-	31.94	-	-	-
C	80.40	-	-	19.60	-	-	-

Patina formed on bronze artifacts, may display complex products and structures. The corrosion mechanism depends on the microstructure of the metal or the alloy, which is attacked by corrosive agents after burial [26]. *Cuprite* (Cu_2O) is typically the first layer of corrosion on the surface of bronze artifacts that are found from soil excavation when a bronze object is corroded [2]. The structure of cuprite is very important considering its effect on the corrosion process in copper alloys. The constructional defect of the oxide compound ($Cu_{2-x}O$) [3] is effective in assessing the migration of ions in the cuprite layer as a semiconductor [4]. The corrosion of the copper-rich phase is observed under oxidation conditions [7]. Tin oxides are observed when tin rich phases are corroded in ancient bronze objects [6]. Based on the tin content and metallic phases, tin bronzes can be divided into low-tin and high-tin groups [27]. The selective corrosion behavior and the formation of tin oxide (SnO_2) are the predictable mechanisms in high-tin bronzes [28]. On the other hand, the main metallic phase in most ancient bronzes is -α solid solution in low-tin copper alloys. However, the formation of different phases in the alloy strongly depends on the cooling rate and the amount of tin, and the formation of α + δ eutectoid matrix in low-tin bronzes with about 10% of tin (as observed in Figure 8 for Ziviyeh artifact–2) is also possible, but this may produce embrittlement in the cast bronze [29-30].

In some bronze objects, a thin corrosion crust was formed on the surface of bronze with a triple-layer structure due to copper leaching from the bronze surface including the internal compact corrosion part, tin-rich corrosion/oxidation product as a noble patina, and the external copper corrosion products [31]. In the corrosion mechanism of a two-phase metallic structure containing the $\alpha + \delta$ eutectoid, corrosion can remove the copper-rich phase and the formation of a fully stabilized tin oxide layer that resists the subsequent groundwater attacks is led by the tin oxidation of the residual part [6, 32]. However, the formation of copper/tin oxides as a uniform film on the surface of the artifacts is attributed to the uniform corrosion in low-tin bronzes in many cases.

Figure 9 shows the changes and transformations of the compounds by the formation of magnetite mosaic products. In this figure, zones A and B show the difference only in the amount of oxygen with semi quantitative analysis of EDX (Zone A: 19.02%; Zone B: 22.76%), indicating that one of the oxide compounds has been probably converted to magnetite (Fig. 9).

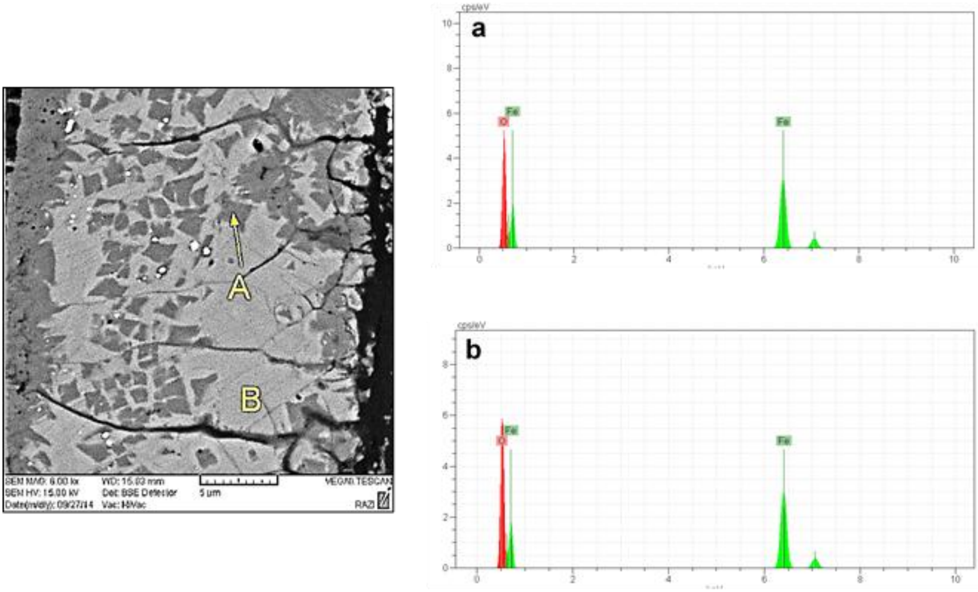

Fig. 9. SEM image of Figure 8-C zone and its oxide phases for Ziviyeh artifact–2

Based on Turgoose theory, it is observed that corrosion products can be more oxidized in corroded iron objects [33]. It is also confirmed that iron oxyhydroxides are converted into a stable magnetite compound with oxygenation in the presence of metal iron [15]. Consequently, in these samples, the formation of magnetite layers can be attributed to the conversion of oxide and oxyhydroxide products as a stable state, which despite the high corrosion of iron retains the overall shape of the daggers in the present form. However, an increase in the volume of the deposited oxyhydroxides on the metal surface and in the oxide layers causes tension, cracks, and finally damage (Figure 10). The volume occupied by a mole of goethite is equal to $21cm^3$, and for lepidocrocite, it is equal to $22cm^3$ [16]. As shown in Figure 10A, an increase in the volume of corrosion products can cause tensions up to 10000psi which results in cracking. This phenomenon is known as wedging [34]. Stress corrosion cracking is created in both intergranular and transgranular corrosion forms. It is observed that intergranular crack can be continued as a grain boundary crack. The presence of holes, pores, scratches on the metal surface acts as tensile points. The stress is mainly aimed at the tip of pores. Stress corrosion cracking often starts from the lower part or the tip of the cavities and the stress is directed to the end sections. A plastic deformation may occur at the close points to the tip of cracks due to the concentration of stresses. The new phase may have different strengths and plastic deformation causes reduction in its corrosion resistance. The cracks in the formed oxide layers create a route for the easier transfer of oxygen and moisture, resulting in conditions for more corrosion, even intergranules causing corrosion in bronze tapes (Fig. 10).

With regard to the electrochemical mechanism of corrosion, oxidation and reduction can be performed at the metal joint with the dense product layers. In the corrosion of iron artifacts, the mechanism of corrosion is controlled by the transfer of the dissolved oxygen in the porosity of corrosion layers, and shortcuts for release are provided by the presence of cracks in these layers [19]. In the presence of chlorides, with the formation of chloride compounds and absorbing moisture, Cl^- ions with rapid transfer of these shortcuts play an important role in accelerating the iron corrosion [35].

A similar behavior is observed in the case of Ziviyeh artifact–1. The oxide products, goethite and lepidocrocite as the main corrosion products, are also higher for this dagger handle compared with copper corrosion products. In addition, copper and tin oxide compounds were observed in the form of a thin layer on the bronze surface (Fig. 11).

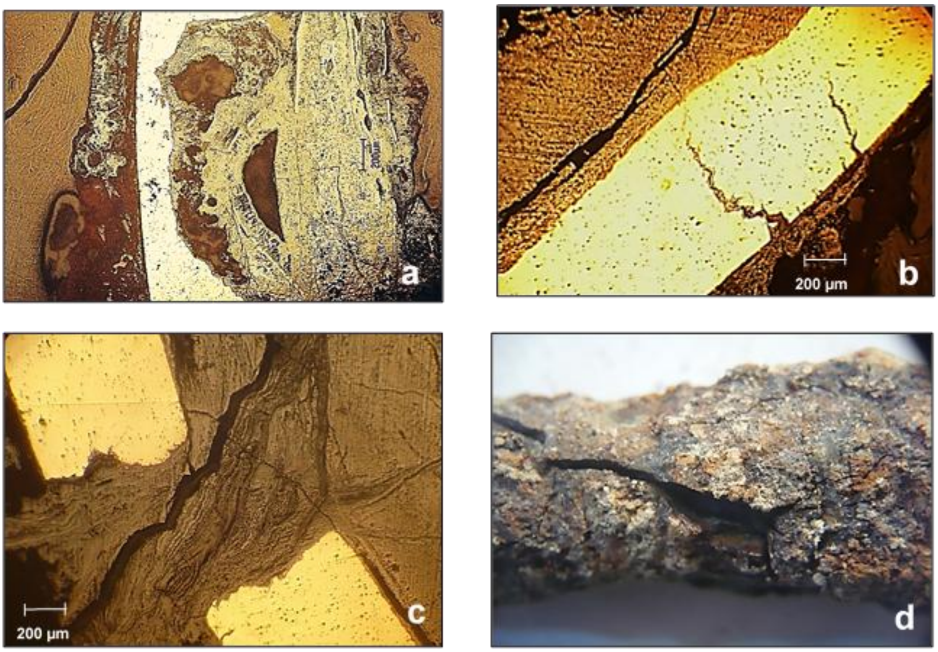

Fig. 10. Optical microscopic (OM) images 12.5X magnification from: a) Increasing volume of iron oxide products; b, c) Creating SCC and fracture in the bronze strip of Ziviyeh artifact–2; d) Apparent evidence of cracks in the same artifact.

The formation of *Ludjibaite*, copper phosphate salt ($Cu_5(PO_4)_2(OH)_4$), based on the results of XRD in Figure 4, on the surface of Ziviyeh artifact–1 is caused by the adjacency of the artifacts with the skeletons in the burial environment.

In addition, the corrosion of iron and the formation of oxide compounds are revealed by the results of the elemental analysis as shown in Figure 12, and it is also confirmed that the iron oxyhydroxide compounds are deposited on the surface of bronze strips (Fig. 12).

The active corrosion of the iron part of the artifact in the present condition is indicated by the holes filled with brown iron oxyhydroxides and the formation of hydrated iron salts on the surface (Fig. 13).

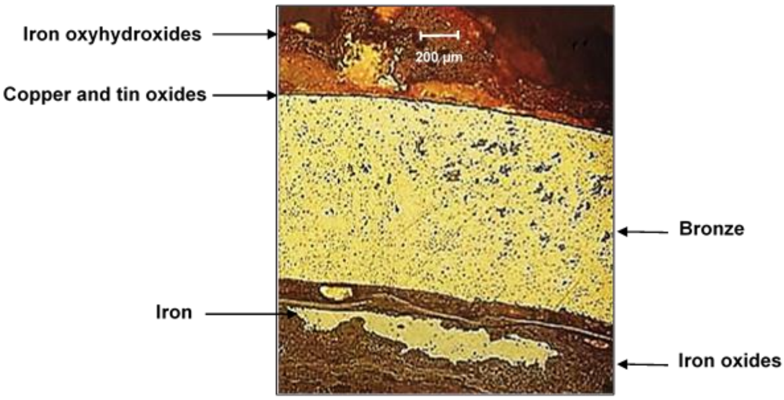

Fig. 11. Polarized light microscope image of oxide layers on cross-section of Ziviyeh artifact –1

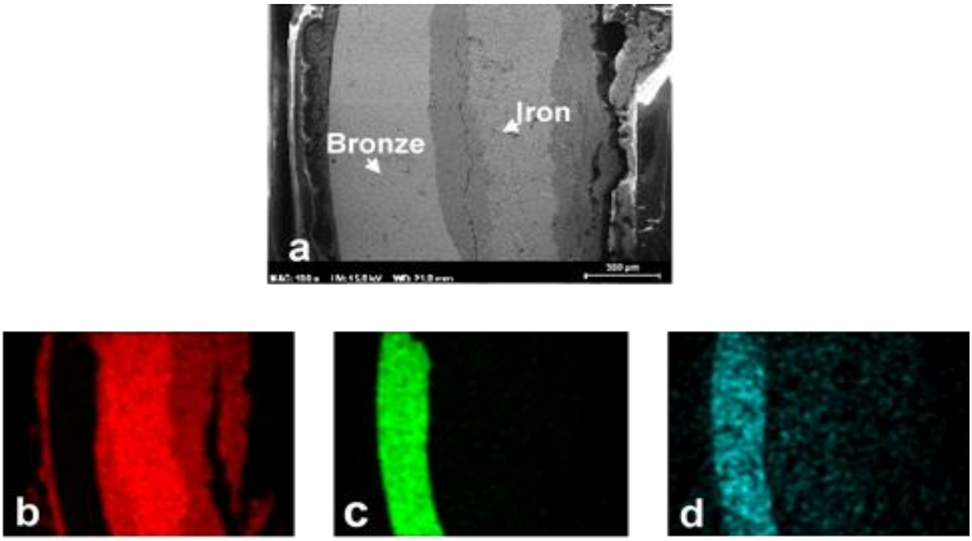

Fig. 12. SEM image and distribution map in cross-section:
a) SEM image as backscatter of a cross-section of Ziviyeh artifact –1,
b) SEM Distribution Map of Iron, c) SEM Distribution Map of Copper, d) SEM Distribution Map of Tin.

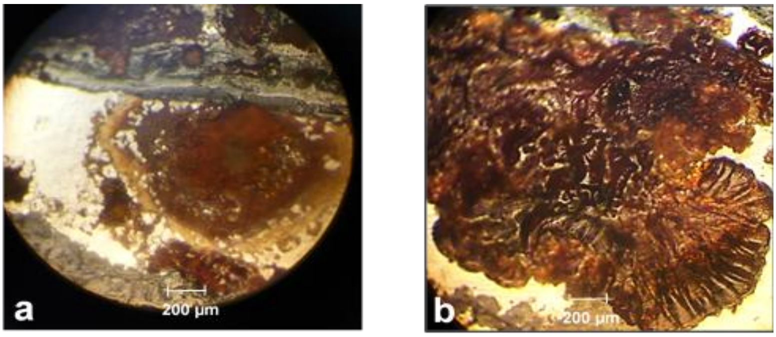

Fig. 13. Optical microscopic (OM) images 12.5X magnification from:
a) Optical microscopic image of the holes filled with brown iron oxyhydroxides,
b) Formation of hydrated iron salts on the surface in Ziviyeh artifact –1.

The process of weeping or sweating and the presence of wet areas with acidic fluid or red hollow bubbles on the surface are the signs of active corrosion in iron. The process of sweating depends on the hygroscopic property of iron salts, especially iron chlorides II and III that form hydrated salts. These salts produce orange fine droplets by absorbing water when the moisture is high. A shell is formed on this liquid and then deposits as iron oxyhydroxides when Fe(II) ions are oxidized to Fe(III) ions. The droplets are completely dried and leave a glossy layer or orange-brown blister (bubble) when the relative humidity is reduced [13].

The concentration of chloride in some parts of the inner layers and the surface of bronze tapes is shown by the distribution of the chloride in the image of the electron scan (Fig. 14).

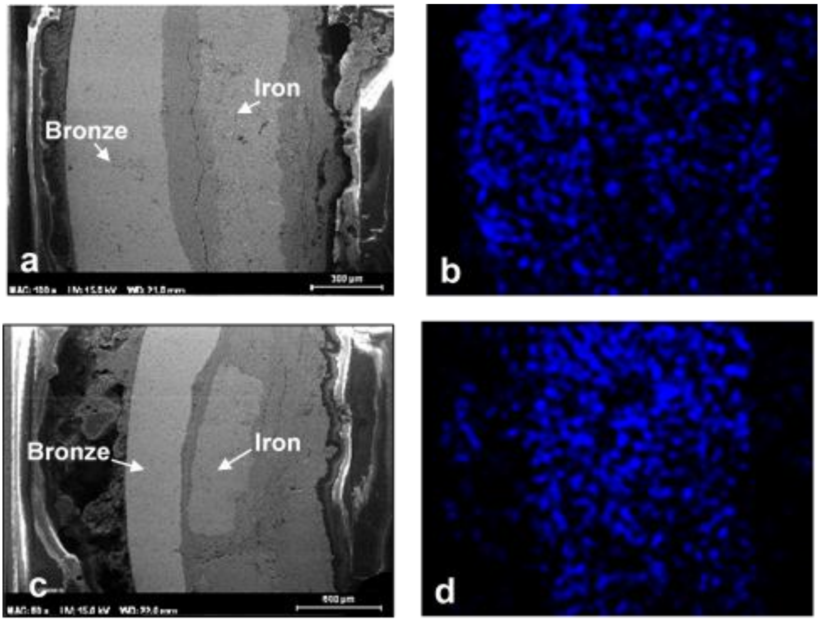

Fig. 14. SEM image and distribution map in cross-section:
a) SEM image of corrosion layers of Ziviyeh artifact –1;
b) Distribution map of chloride in Ziviyeh artifact –1;
c) SEM image of corrosion layers of Ziviyeh artifact –2;
d) Distribution map of chloride in Ziviyeh artifact –2

The formation of secondary green/blue products on the surface of bronze tapes is due to the reaction of copper with soil carbonate despite the strong influence of chloride on local corrosion and the formation of the cavity in the process of corrosion of the ferrous parts.

It is clear that the concentration of chloride is not relatively high in the burial environment as well as corrosion layers due to the formation of the oxyhydroxide of *lepidocrocite* and goethite along with the thick layer of magnetite and lack of the formation of akaganeite as a final product of oxidation, which is observed as the only product at high concentrations of Cl^-. The compounds such as *lepidocrocite* (γ-FeOOH), *goethite* (α-FeOOH), and *magnetite* (Fe_3O_4) are formed at low Cl^- concentrations [16].

Conclusion

Based on the results of this study, the main body of the two dagger handles with decorated strips covered by corrosion products is made of iron. The corrosion behavior of iron at the copper-iron junction point is accelerated by the bonding of two different metals of iron and copper. The oxyhydroxides of goethite and lepidocrocite were formed in different parts of the sample. The formation of gray magnetite oxide has caused the main form of the artifacts to remain despite the high corrosion. Severe stresses on bronze strips have been caused by the formation of oxyhydroxides and the increase in their volume. Stress corrosion was observed along the grain boundaries of bronze strips, which caused cracks and fractures, despite the cathodic protection of bronze parts from the galvanic corrosion of iron at the copper-iron joint. The shortcuts for the transfer of moisture and anions are provided by these cracks in the magnetite layers. The layered structure has been formed by the oxide and oxyhydroxide compounds in some parts, and the conversion of compounds into a stable mosaically form of magnetite was also observed. In addition, a long period of corrosion in the burial environment and the conversion of iron oxyhydroxide products into stable magnetite are indicated by the formation of a layered structure of stable magnetite iron oxide and iron oxyhydroxides. The results have also shown that chlorides have been effective locally in the localized corrosion process at some specific points. The formation of the hygroscopic iron corrosion products and the generation of wet blisters along with the cavities filled with brown iron oxyhydroxides indicate the active atmospheric corrosion of the main body of two Ziviyeh artifacts. Copper and tin oxides are the main products formed on the outer and inner surfaces of the strips due to the uniform corrosion of bronze strips, and they are formed as a thin layer that has been coated on both surfaces with iron oxide and oxyhydroxide products. In addition, the local formation of green and blue compounds of copper basic carbonates is attributed to the sequestration of calcium carbonate compounds in various parts of the artifacts and their reaction with copper in bronze strips.

Acknowledgements

The authors appreciate specialists at the Research Center for Conservation of Cultural Relics (RCCCR), Tehran, Iran, for preparing the radiography and microscopic images, central laboratories at Sharif University of Technology, Tehran, Iran, for instrumental analysis and Razi Metallurgical Research Center, Tehran, Iran for performing SEM studies. The authors especially thank Y. Hassanzadeh, an archaeologist at The National Museum of Iran.

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Received: October 05, 2017
Accepted: June 10, 2018