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Identifying the Technology of a Bronze Dagger Discovered in Espidezh Region of Bazman in Sistan and Baluchestan, Iran

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Abstract

Espidezh is historical cemetery and main heritage of Baluchistan with an area of 25 hectares. It is one of the most important settlement centers of the pre-history era. Numerous bronze monuments and objects with multiple applications have been obtained from this archaeological site. One ofthe discovered artifacts is a bronze dagger belonging to the early second millennium BC. In the present study, the intended dagger is analyzed using metallographic microscopes (OM), scanning electron microscope (SEM-EDS), X-ray diffraction (XRD), and radiography. The results and data obtained from device analysis of the dagger indicated Copper-Arsenic alloy (Cu- As) which hasbeen made using casting method. The existence of Cuprite, Tenorite and Paratacamite phases indicated the variable environmental conditions which had resulted in the brittleness and flimsiness of the bronze dagger.

Key words: Espidezh, dagger, bronze disease, Cu-As alloy, XRD, SEM-EDS

1. Introduction

Espidezh, the historical cemetery and beating heart of Baluchestan heritage, is one of the most important settlement centers belonging to prehistory era and is located 40 kilometers away from southwest of Bazman town in Iranshahr city. Espidezh with an area of approximately 25 hectares includes the monuments of two distinct eras of Islamic and prehistory periods (Figure 1). The Islamic periods includes the remnants of a stone castle, stone fortifications and tombs and are generally located in the southeast of the area. The prehistory monuments belong to two shorter time periods, that is, the third and second millennium BC and beginning of the Iron Age. Among the outstanding discoveries of Espidezh cemetery, it can be referred to all kinds of potteries(Figure 3), stonework (Picture 4), and metalwork (Figure 5), statuettes and decorative beads(Figure 6), different kinds of stamp beads, agricultural implements and… Likewise, the role of human on clay dishes emerges for the first time in Sistan and Baluchistan (Figure 7). One of the most significant data of Espidezh discoveries is the metal objects, 99.5 percent of the objects are made of bronze (Heidari, 2005). Considering the results of the discoveries, it can be asserted that the primary settlers of Espidezh in the second and third millennium BC have high level of knowledge and technology in various fields and they have also taken the benefits of social welfare. At that time, divisions of labor has taken place and technical jobs and professions such as, masonry, tool-making, metalworking, pottery, trade, were created. They used stump beads which were made of stone or metal to establish their ownership. The size, role, and the beads' material indicated the rate of social credit of their owners.

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Figure 1: The location the site in South-East of Iran

Figure 2: Excavating in the Espidezh area (Heydari)

Figure 3: A pottery, Espidezh, (Reference: Mohammad Heidari), Figure 4: Astonework, Espidezh,

(Reference: Sistan and Baluchistan cultural heritage), Figure 5: A metalwork, Espidezh, (Reference: Mohammad Heidari), Figure 6: A-Statuettes, B- decorative beads, Espidezh, (Reference: Sistan and Baluchistan cultural heritage), Figure 7: Painted pottery, Espidezh, (Reference: Sistan and Baluchistan cultural heritage)

The artifact under investigation in the present study is a dagger with copper base which was discovered in depth of185 cm in burial number 101 in cemetery A located in the central part of Espidezh area in 2002 (Figure 8).

Figure 8: Burial 101 (The dagger under investigation besides other stone and clay works) (Reference: Mohammad Heidari)

The dagger has a length of 32 cm, maximum width of 4.3 cm and primary weight of 121.43grams. According to the chronology studies which were conducted based on the study and implementation of cultural affinity of Bronze Age in the districts of southeast of Iran (Bampour, Shahr-e Sukhteh, Shahdad, and Espidezh). It is almost 1500-2500 BC. Unfortunately, although12 years have passed from the discovery of Espidezh area in Baluchistan, not scientific study and exact examination have been conducted on the discovered data in line with identifying the buried culture and civilization of the area. In the present study, the technical study of the aforementioned object has been emphasized. Considering the need to study damages with the purpose of preservation and restoration of the object, the destructive corrosions products were studied.

Figure 9: the top view of the object under-study (Reference: Authors), Figure 10: the bottom view of the Object under-study (Reference: Authors)

2. Methodology and instruments

In the present study, in order to investigate the construction method, identifying the elements used in its construction process, and studying the type of corrosion products, the object was putto microscopic study and device analysis including scanning electron microscope, X-raydiffraction, and radiography. Metallographic studies were performed in order to investigate the corrosion layers' sequence in restoration laboratory of the Arts Faculty of Zabol. The object under investigation has green-colored corrosion in all its length, while the black-colored corrosions and hard mud deposits were more observed at the blade of the artifact. The corrosion on the edges of the object, especially at the blade, was so intense that the edge looked like a burned wood and would be powdered and poured down even with a little shake. There were some cracks in the object, the depth of the cracks were more at the handle than other places. The human damage that were observed in the object could not be ignored, like the unprincipledsticking of the object by using an industrial glue in 4 to 5 areas in the length of the object which had taken place due to the old fractures that may have resulted from moisture fluctuations, and another case was registering the property number using the red marker directly on the handle ofthe object (Figure 10). This object is currently held in the big museum of Zahedan.

2.1. Testing methods

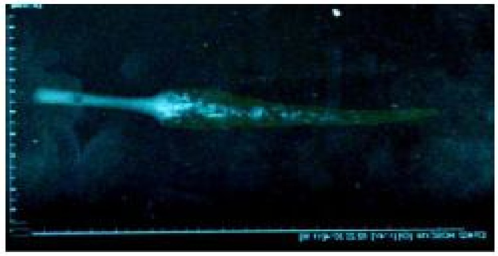
For elemental analysis and structural identification of the object, scanning electron microscope (SEM), VEGALL model made by PESCAL Company of Czech Republic along with Energy dispersive X-ray spectroscopy (EDS) RONTEC model made by Germany and the Software of QUALTAX model QX2 in Razi Metallurgical Research Center were utilized. Identifying thetype of corrosion products was performed in Kansaran Binalood Company in Tehran by using XRD device (dispersive X-ray method) made by PHILIPS Company (Netherland) and ModelPW1800. X-ray images with the purpose of pathology (the corrosion infiltration) were prepared in radiography laboratory of Amir-Al Momenin hospital in Zabol.

3. Results and discussions

3.1. Radiographic studies

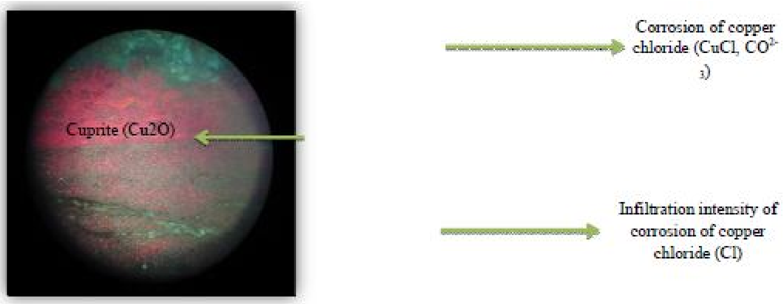
The X-ray radiography was prepared with the purpose of pathology and technique identification of the work, and presents information such as construction method, decoration performance, connections types and … (Stuart, 2007). In order to identify the construction technique of the artifact and the infiltration rate of the corrosions, the radiography images were provided (Figure11).

Figure 11: The radiography image of the object under investigation



The radiography image indicated a little metal core in the object and is a sign of the intensity and infiltration of its corrosion. Corrosion is more intense in the blade of the dagger. The cracks and fraction areas of the object are hidden under the bulky corrosion products. Likewise, in the radiography images, the integrity of the object is recognized and no joint points were witnessed in it. The existence of a hole in the dagger's handle might be the result of connecting the handle for the dagger. The object under study did not have the necessary metal core for performing metallography with the purpose of recognizing the Microstructure, hence, metallography was conducted with the purpose of investigating the sequence of corrosion layers(Figure 12), and in order to identify the construction technique, the physical features of the artifact, such as the existence of the available evidence at the end of the handle, were emphasized(Figure 13).

Figure12: Sequence analysis of the corrosion layers under a Metallography microscope Before H (X 100)



Systematic identification and analysis associated with construction techniques of metal artifacts is primarily based on the analysis of the artifact. But in specific occasions, considering the formation of the corrosion layers on the ancient metal artifacts, also complete corrosion of the surface, scientific systematic analysis cannot be conducted in some cases. Hence, for understanding the construction technique of artifacts which have had intense corrosion, decision can, to some extent, can be made on the basis of physical features. Regarding the intended object, due to complete corrosion of the surface and the impossibility of taking sample from the metallic core for determining the construction technique, no definitive theory can be presented for its construction method. However, the evidences show casting at the end of the object's handle which indicates the mold casting technique; because at the time of pouring the molten material into the molds, the molten material has ended, cooled, and produced some protuberance(probably caused by casting port) (Figure 13). Likewise, the symmetric and even surface of both sides of the object indicates the utilization of a two-sided cast in construction of the intended artifact.

Figure 13. A-B: The hard protuberance at the end of the handle

3.2. Device studies XRD

XRD device is a device analysis system that is utilized in determining the phases in samples suchas soil, concrete, clay, alloys, and corrosion products (Stuart, 2007). Diagrams 1 and 2 are information that this device has given us regarding the corrosion products of the object under investigation: black-colored products include the corrosions of "Tenorite (Scott, 2002, 95) and Atacamite. Likewise, calcium carbonate and gypsum related to residues caused by the environmental burials were discovered (Table 1).Green-colored products included corrosions of Atacamite, Paratacamite, and Chloride Cuprite (Scott, 2002, 123). Likewise, Illite and gypsum which are probably related to environmental landfills were discovered (Table 2).

Table 1: identified primary and secondary phases in black-colored corrosion products (Diagram 1)

Chemical composition	Primary Phase	Secondary phase
(CuO) Tenorite	+	-
($CaCO_3$) Calcit	-	+
($CaSO_4.2H_2O$) Gypsum	-	+
Cu_2 $(OH)_3Cl$ Paratacamit	-	+

Table 2: identified primary and secondary phases in green-colored corrosion products (Diagram2)

Chemical composition	Primary Phase	Secondary phase	Trivial phase
$Cu_2(OH)_2Cl$ Atacamite	+	-	-
$Cu_2(OH)_3Cl$ Paratacamite	-	+	-
$CaSO_4.2H_2O$ Gypsum	-	+	-
$CuCl_2$ Cupric Chloride	-	+	-
(KH_3O) Al_2 Si_3 Al $10(OH)_2$ illite	-	+	-
$CaCO_3$ Aragonite	-	-	+

Diagram 1: Black- colored corrosion products

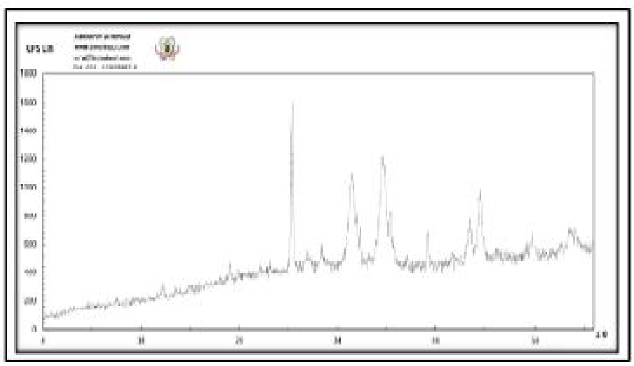
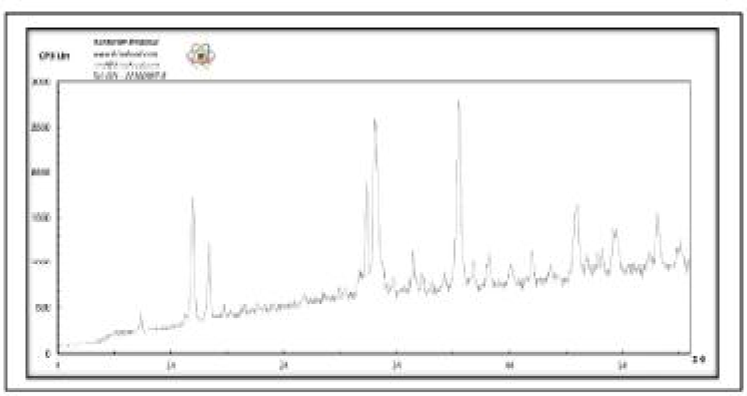


Diagram 2: Green-colored corrosion products



The results of XRD analyses indicated active corrosion or bronze disease in the samples. Bronze disease can be considered as the process of reaction of copper with chloride ion, the formation of nantokite and finally changing to one of the Copper trihydroxyl chloride, on exposure to air and moisture, inbronze artifacts and other copper alloys (Scott 1991).In alkaline conditions, the first layer which forms on copper base alloys is cuprite. But in acidic conditions, cuprite, Atacamite, and Paratacamiteare formed, respectively. The main cause of bronze disease is chlorine or Nantokite. This element, it is in the absence of water, is very stable and protect the object like Pathein layer; however, in case of moist, it is immediately activated and causes the bronze disease (Oudbashi, Imami, and Davami, 2011). The reaction products are copper trihydroxyl chloride and soluble ions. Simultaneously, the corrosion process remains with the reaction between chloride ion (or hydrochloric acid) and metallic copper and continues with the formation of copper chloride (I) (Nantokite). In the presence of water and oxygen, Nantokite changes to copper trihydroxyl chloride. In the presence of moisture and oxygen, this process continues until the complete transformation of metallic copper to coppertrihydroxyl chloride (Scott, 1991).

The long term conditions of burial environment and also bronze objects' corrosion in the soil cause the occurrence of interesting events: Bronze can completely change at the time of burial and change to corrosion products, or with a thick and wide corrosion it can form soil minerals while an outstanding amount of its metal remains, or it may be covered with a thin, shiny and beautiful Pathein layer. These differences to a great extent depend on the soil environment and its corrosion (Plenderleith, 1898). The amount of corrosion in most of the bronzes obtained from the soil can be from a very thin Pathein layer to the complete corrosion of the metal. Like Diagram 2 (Atacamite, Paratacamite, and Tolbachite) can be formed at the surface of the metal and likewise Diagram 1 copper corrosion products (II) such as (Tenorite and Atacamite) are formed on the copper compositions (I), the chemical compositions of the copper corrosion products (II) depend on the anions present in the soil environment and on their concentration (Robbiola et al. 1998). According to the results of the analyses, it can be concluded that the occurred corrosion in the dagger is due to presence of chloride ion in the environment which has resulted in bronze disease. Identifying the compositions of copper chloride in the corrosion products confirm this process.

3.3. Studying the object structure with scanning electron microscope (SEM-EDS)

Elemental analysis using scanning electron microscopy equipped with elemental analysis system (SEM-EDS) was conducted on the intended case. The results of elemental analysis indicated that the main base of the intended metal is copper-arsenic.

Figure 14:Cross-section SEM image of handle dagger belonging to Bazman Espidezh (500 μm)

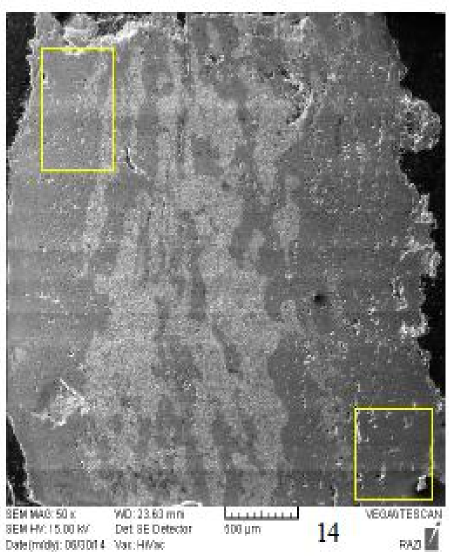
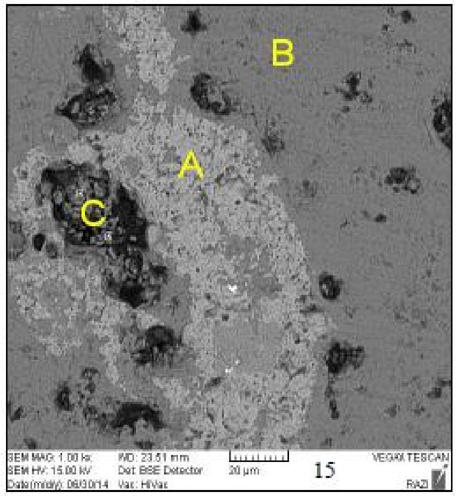


Figure 15: SEM image of the artifact's cross section (200 μm) of the dagger (Figure 14), the existence of light and dark densities indicates two different phases in the case's surface.



The existence of small holes in the darker phase is completely observable, which is the result ofthe gas emission from the metals' surface (Matrix). Considering the EDS analysis from the metal body matrix, it was found out that the case has complete corrosion. The existence of chlorine indicates the bronze disease in the case. The main base of the intended metal is copper-arsenic. In the ancient world, for integrating the alloys and gas emissions, the arsenic metal has been utilized (Ehsani, 2003).In Figure 15, which has been displayed with the magnification of 200, the analysis of three points of A, B, and C on the section of the object of study by EDS analyst indicate that (Table 3).

Table 3: the non-normalized results of (unn. C) Analysis of SEM-EDS [wt.%] from cross section of the handle dagger belonging to Espidezh of Bazman

Element / Location	Carbon	Oxygen	Chlorine	Copper	Arsenic	Calcium	Palladium	Silicon
Metal body	2.63	12.46	8.72	72.75	1.60	-	-	-
Area A	-	10.34	5.11	82.56	-	-	-	-
Area B	1.90	15.67	15.78	62.37	5.38	0.92	0.42	-
Area C	13.51	14.11	7.97	41.15	2.76	1.35	-	1.26

In area A, the EDS data indicated the lighter grey phase, which are possibly related to copper chloride corrosions. Corrosion at this point is intense (Figure 15). In area B which is taken from the dark area, the metal core has chloride compositions, which indicates weakness and lack of strength needed for the intended sample. Corrosion at this area is intense. Some amounts of Palladium can be observed in this sample (Figure 15).In area C, which is a darker area and some holes can be observed in this area. This area has some amounts of chlorine and deposits of other minerals. At this point, carbon can be witnessed in large amount (Figure 15).

4. Conclusions

The results of SEM-EDS indicated that the main base of the intended dagger is copper-arsenic. Considering the evidences of casting at the end of the object's handle, this indicates the mold casting technique for its construction. The symmetric and even surfaces of both sides of the dagger, and its integrity which was observed in the radiography images indicated the utilization of two-sided mold in construction the object. Considering the radiography and metallography studies, the infiltration intensity of the object was determined.

In the results of XRD device studies, the green-colored corrosion products were identified to be Atacamite (Cu2Cl (OH)), Paratacamite (Cu2 (OH) 3Cl), and Tolbachite (CuCl2). The black-colored corrosion products included Atacamite (Cu2Cl (OH)) and Tenorite (CuO). Based on the results of XRD analyses, it can be concluded that the occurred corrosions in the dagger are due to the existence of chloride ion in the long term conditions of burial environment and as a result the occurrence of bronze disease. Identifying the copper chloride compositions in the corrosion products in the XRD device studies and also identifying chloride ion in EDS' analysis from the metal body matrix approves this process.

5. Acknowledgements

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