EUROPEAN JOURNAL OF MATERIALS SCIENCE AND ENGINEERING
Volume 7, Issue 4, 2022: 288-298 | www.ejmse.ro | ISSN: 2537-4338

DOI: 10.36868/ejmse.2022.07.04.288

METALLOGRAPHIC STUDIES OF IRAN'S IRON AGE: CASE STUDY BRONZE PIECES FROM JEYRĀN TEPE, OZBAKI

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Abstract

This study is a report of the results of metallographic study of 5 bronze pieces found in Jeyrān Tepe dating back to the Iron Age II. Jeyrān Tepe is located 250 m southwest of Ozbaki as one of its hills. The obtained metal pieces included bracelets, necklaces and hairpins, which were used for decoration. The objective of this article was to identify the process of bronze production and study the structure and composition of the components of metal pieces, Iron Age in Jeyrān Tepe, based on laboratory studies that have addressed questions in the field of elemental compositions and the method of bronze production in the study area. For this purpose, five bronze pieces were studied using vegetative electron microscope with scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) analysis, metallographic studies at 200 × magnification and X-Ray diffraction (XRD) to identify the chemical composition, metal production technique and type of alloy. The results of XSEM-EDS on the metal background of the samples showed that the constituent elements of these metals are oxygen, copper, tin, silicon, chlorine, sulfur, aluminum, magnesium and carbon. The main reported elements are copper and tin, so metals are made of pure copper and copper-tin alloys. The different amount of tin in bronze pieces of Jeyrān Tepe could be due to uncontrolled extraction and alloying methods.

Keywords: *Metallurgy, Ozbaki, Iron Age II, SEM-EDS, XRD.*

Introduction

Processing different metals is very important in cultural processes and human technology. The importance of the formation and evolution of the knowledge of metallurgy in the ancient times is common to ancient metalwork (archaeometallurgy), as far as it has influenced the division of prehistoric cultural periods in the 19th and 20th centuries AD and is considered as a basis for division in this era. Ancient metalworking process occurred for the first time in Anatolia, Caucasus, Iran and Levant [1]. The Iranian Plateau and its residents can be enumerated as one of the pioneers in progress of technology, science and knowledge in the ancient world. The development of metallurgy on the Iranian Plateau has been a topic of interest to both archaeologists and scientists for many years because of the remarkable history of the metallurgical activities in this region and concerned the wide variety of the technologies, compositions, innovations, etc. in Iran, raw materials for metalworking have been provided by searching and preparing natural copper, extracting metal from ore and mixing metals to produce alloys. The Iranian Plateau has a significant history in the metallurgy of copper and its alloys in the prehistoric period.

The first natural copper found in from the southwest of Iran in the Deh Luran Plain in the Ali Kosh Tepe and the Zagros foothills. The ancient metalworkers used native copper to manufacture small decorative objects [2]. In Zagheh and Mushaki Tepe, metals obtained from

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natural copper are made by heat treatment method [3-4]. Kerman is considered as the richest copper region in Iran. So, many ancient mining centers have been identified in the eastern and southeastern Iran, the highlands, the Kerman Plain and the Lut Plain [5]. The remains of old mining in Yahya Tepe have led to the dating of mining and extraction operations of copper from Sar mine around 3000 BC [6].

In Yahya Tepe, the process of metalworking with pure natural copper and alloyed copper has also been identified [7-8]. The discovery of metal smelting plants in Tel Iblis shows the metamorphosis of sulphide copper ore in 4000 BC and the prevalence of complex operations of smelting and metamorphosis of ore and metal extraction there [9]. Also, ingots were produced in the beginning of the 4th millennium BC [3]. In the Bronze Age (late 4th millennium and early 3rd century BC), metal ingots were produced in the form of alloys based on tin and arsenic [10] and their samples have been provided in the Bronze Age centers of the Iranian plateau, and Southeast of Iran [11-12]. metallurgical processes were extended by smelting copper oxide ores in crucibles during 4th and 3th millennium BC. The chalcolithic period (ca. 4500-3000 BC) is the period of emergence and development of smelting of oxide and then sulphidic copper ores in small scale, as it was discovered in Arisman, near Kashan.The metallurgical technologies during the late chalcolithic period (ca. 3500-3000 BC), is a mixture of crucible smelting and furnace smelting. It is worth noting that the main metallic composition in the Chalcolithic period is arsenical copper that may has been produced accidentally by smelting As-bearing copper ores leading to obtain metallic copper with significant amounts of arsenic. Nevertheless, some evidences of intentional arsenical copper production have been found during late Chalcolithic and early Bronze Age archaeological sites, such as Arisman [13].

The third millennium BC was occurred with occurrence of a new alloy, tin bronze. Early evidences of this technology were observed in western Iran, Luristan at the beginning of the third millennium BC. Some tin bronze objects with significant amounts of tin were detected among copper and arsenical copper objects discovered from Early Bronze Age graveyards such as Kalleh Nisar and Bani Surmeh [4-14]. Studies on Iron Age bronzes in western Iran have shown that arsenic has been identified as a minor element or particle in many samples [15-14].

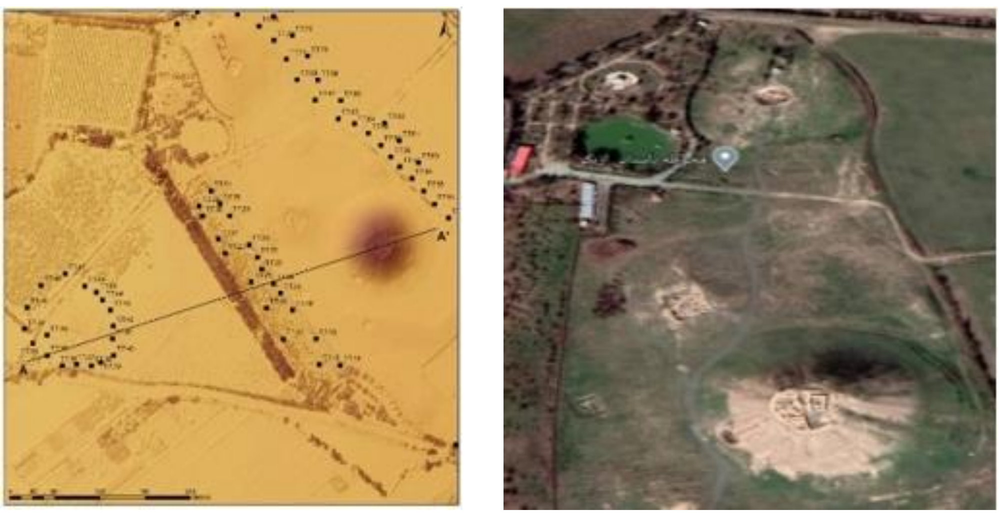
Early evidences of tin bronze metallurgy have been occurred in the third millennium BC but this technology was limited for about 1000 years in western and south-western Iran. Results of analytical studies revealed that the main copper base metallurgy has been copper and arsenical copper in other regions of the Iranian Plateau during the third millennium BC. Tin bronze was emerged in central Iran during the middle and late Bronze Age (ca. 2500-1500 BC) such as evidences from Malyan (Fars) [16]. Therefore, no evidence of tin bronze has been observed in eastern Iran, even at the mid of the second millennium BC. Although tin bronze was occurred during the early Bronze Age and was spread during middle and late Bronze Age in western and central Iran. With the beginning of the Iron Age around 1500 BC. The use of bronze alloy continued. Bronze can be considered as a common alloy in making decorative and functional objects in the Iron Age of the Iranian Plateau (550-1500 BC) [3]. According to the results of archaeological studies, the use of bronze alloy is common especially in the north, west, and northwest of Iran, and many bronze objects have been obtained from the Iron Age sites of these regions [17].

Laboratory studies of the metal objects of Marlik Iron Age cemetery [18] show that the objects are made of tin-bronze alloy and the amount of tin varies between 2 and 13which show that the alloy used in the items of the Marlik cemetery was a two-component tin bronze alloy [18]. Laboratory studies of the Lorestan bronze objects also show the high quality of production and construction of various objects using bronze alloy in this period. Laboratory studies on some areas of the Pishkoh Lorestan show the use of tin bronze alloy with different tin content in the production of various decorative items and bronze vessels [19-20]. As mentioned, most of the studies are related to the west of Iran and tin bronze technology was less common in eastern Iranian Plateau during Bronze Age until in 2020 analytical study on a series of copper alloy objects excavated from the Bronze Age site of Shagak-e Firouzeh, Neyshabur (north- eastern Iran). Result show that the prevalent copper-base metallurgy in the site was unalloyed and arsenical copper in general and arsenical copper was the main metallic material used in other parts of the country, in central and eastern Iran in particular [21] Therefore, studies show that studies metals constitute an essential part of the development of societies from Neolithic period until the iron age and approximate dates for the beginning of these technologies are copper (6000 BC), bronzes(3500BC) and Iron (1500BC) [22].

One of the positive points the conducted studies is the evolution metallurgy in ancient societies but these studies mostly focus on the analysis of the obtained works and less mention is made of their mineral and production documents [23]. Almost all the early tin bronzes that have less than 5% tin can be considered as those made from copper ores containing limited amount of tin. Because studies have shown that the copper ores of the Middle East contain about 1-6% of tin [24]. The objective of this study was to identify the type of alloy and determine the elemental compositions in metal pieces to investigate the metallurgy of metals belonging to the Iron Age II of Jeyrān Tepe.

Study area

One of the archaeological sites in the north of the central plateau of Iran is Tepe Ozbaki. The site is located in 50.34 degrees longitude and 35.58 degrees latitude, 85 km northwest of Tehran, near Savoojbolagh, 15 km southwest of the old Hashtgerd, and about 2 km west of Asadabadi, in the northeast of Ozbaki village. Ozbaki Tepe and all its hills are about 1200 ha, which were regularly and continuously excavated since 1998 to 2002 during five periods by Yusuf Majidzadeh. Based on the remains obtained, three cultural pre-history cultural, historical and Islamic periods were identified in this area. In the summer of 2017, the Ozbaki area was re-examined and explored by Ruhollah Yousefi. One of the hills related to Ozbaki Tepe is called Jeyrān Tepe, which is located about 250 m southwest of Ozbaki Tepe (Fig. 1) and in the third period of exploration by Majidzadeh, remains of three cultural periods, Islamic, Iron Age and Prehistory identified in it. In this area, 95 burials were found. 49 burials belong to the Islamic era and 46 burials belong to the Iron Age [25].



a) b)

Fig. 1. a) Digital map of Jeyrān Tepe; b) Aerial image of Tepe Ozbaki (Google Earth) [26]

The metal artefacts found in Jeyrān Tepe belong to the 2nd millennium BC (Iron Age II), which were found in two graves in recent excavations (2017) [26]. Very worn and destroyed bones were also found in these graves along with three pottery vessels.

Scientific and targeted studies on new discovery of metal works are very important for reviewing the progress and evolution of the ancient metalworking industry. Given that no independent study has been conducted on the knowledge of the technology of bronze pieces of Jeyrān Tepe, it is important to study and review these works. The objective of this article was to present the results of the laboratory study of five pieces of bronze pieces of the Iron Age II obtained from Jeyrān Tepe and study the structure and composition of the components of the pieces to identify the production process of bronze. The hypothesis of this research is elemental analysis of these pieces and the measurement of their constituent compounds will contribute to increase our knowledge about the ancient metalworking industry in this part of Iran.

Methodology of Production

Materials

To study chemical composition analysis some Jeyran Tepe bronze artefacts, five metallic samples were selected for experiments. The selected samples from excavations carried out by Yosefi Zoshk from 2017. The samples include bronze bracelet, armband, necklace, and hairpin that were used for decoration (Fig. 2).

Fig. 2. Five bronze samples from Jeyran Tepe

Methods

First, for cleaning, the samples were placed in a Pyrex of cold water containing 100 g of dilute sulfuric acid to soften the surface sediments. Then, the softened sediments were removed from the piece using a soft brush and finally washed with distilled water. The selected samples were mounted in epoxy resin. Then, were analyzed by SEM-EDS, SEM (LEO 1450 VP) in the central laboratory of Ferdowsi University, Mashhad. To identify the elemental composition, EDS (Oxford Co. model 7353) with a resolution of 133 EM (electrovolts) was used. Then, the samples were tested by XRD. For this purpose, about 1 g of the sample was separated by a jewelry saw and powdered for analysis.

Results and Discussion

To identify the chemical composition of metal samples from Jiran Tepe, XSEM-EDS analysis was performed on different cross-sectional layers of the samples (Fig. 3) from the innermost layer (A) to the outermost layer (D). The point analysis of the samples was done to identify their composition. Therefore, abbreviations A and B indicate the inner layer and abbreviations C and D indicate the outer layers. The inner layers (A) are rich in copper and the ratio of Cu/Sn, Cu is higher. Layers (C) are rich in Oxygen, which is related to metals corrosion. The results of the metal background of the samples based on weight percentage are shown in Table 1. The constituent elements of these metals are copper, tin, oxygen, silicon, chlorine, carbon, strontium and aluminum (Table 1).

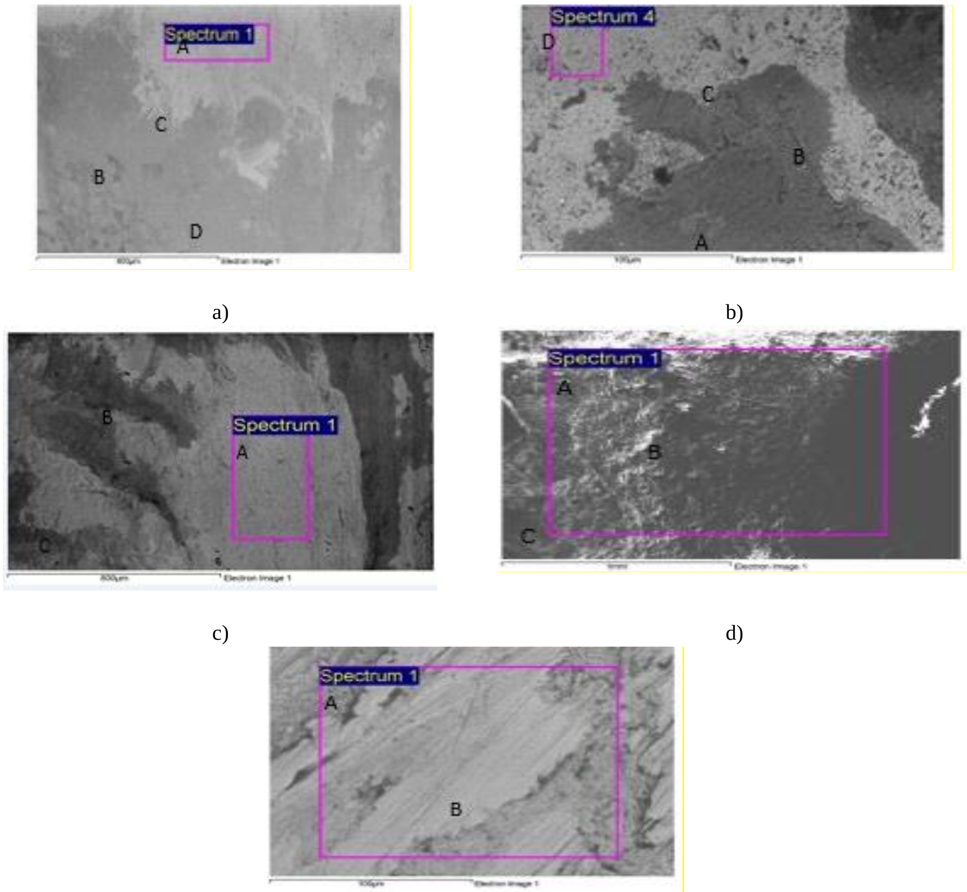


Fig. 3. SEM – EDAX analysis on multiple points from the surface of the analyzed samples: a) sample 1; b) sample 2; c) sample 3; d) sample 4; e) sample 5; f) sample 6.

Table 1. Results of SEM-EDS Analysis on the Samples (%wt)

Sample and zone	Cu	Sn	O	Si	Al	Mg	Cl	C	Sr
Sample 1: zone A	59.05	14.73	24.68	1.54	---	---	---	---	----
Sample 1: zone B	66.77	8.06	21.81	3.36	----	-----	----	---	----
Sample 1: zone C	55.48	6.46	20.95	2.48	------	-----	----	14.63	-----
Sample 1: zone D	58.28	11.01	25.94	3.67	----	-----	1.10	---	---
Sample 2: zone A	67.09	3.73	14.80	---	-----	-----	-----	13.35	-----
Sample 2: zone B	38.62	1.02	35.08	-----	1.03	-----	-----	--	12.14
Sample 2: zone C	69.21	----	13.94	------	1.12	-----	-----	15.73	----
Sample 2: zone D	84.48	----	13.92	-----	1.60	----	-----	---	----
Sample 3: zone A	53.51	8.32	25.97	---	----	0/84		27.01	-----
Sample 3: zone B	28.86	---	34.74	0.87	---	---		23.68	-----
Sample 3: zone C	25.34	---	38.05	---	0.97	---	---		--
Sample 4: zone A	34.25	---	35.08	12.14	1.03	---	---	17.50	---

Sample and zone	Cu	Sn	O	Si	Al	Mg	Cl	C	Sr
Sample 4: zone B	69.21	---	13.94	---	1.12	---	---	15.73	---
Sample 4: zone C	84.48	---	13.92	----	1.60	----	---	--	---
Sample 4: zone D	56.54	1.49	18.27	0.98	--	---	--	22.39	---
Sample 5: zone A	56.14	10.29	16.58	---	----	----	---	17.00	---
Sample 5: zone B	55.85	10.22	16.55	---	----	---	---	17.38	-----

The results showed that the studied metals are divided into two categories: samples 2 and 4 which are made of pure copper and samples 1, 3 and 5 which are made of bronze alloy (copper and tin). The amount of copper in copper pieces is between 34.25 and 84.48% and the highest amount of copper was identified in the innermost layers. Other elements in the copper samples included silicon, aluminum, oxygen, carbon and strontium. The amount of tin in these samples is between 1.02 and 3.73%. In bronze alloy metals, the amount of tin varies between 6.46% and 14.73%, and the amount of copper in these samples varies between 25.34 and 74.11%. Other elements in these samples include chlorine, carbon, silicon, aluminum, magnesium and oxygen. A shown in Fig. 4, the analyzed samples are divided into two completely separate groups. As mentioned earlier, the first group includes metals made of tin-copper alloy, and the second group includes metals made of pure copper. As shown, in almost all alloy samples, the weight percentage of copper is higher than that of tin, and it can be seen that the average change in copper is between 35.90 and 64.85% and the average change in tin is also between 1.49 and 10.43%. Also, in pure copper samples, the average weight percentage of copper varies between 62.65 and 64.85%, and after copper, the most frequent impurity is related to oxygen, carbon, and silicon.

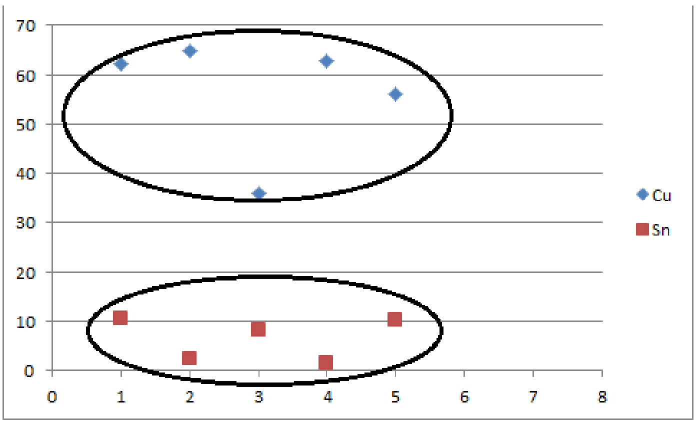


Fig. 4. Changes in the Average Weight Percentage of Tin to Copper in the Analyzed Samples

As mentioned earlier, the results of SEM-EDS analysis on the different cross-sectional layers of the studied samples showed that the percentage of tin in the alloy samples was between 6.46 and 14.73%, and other metal elements were rare identified in the composition. The difference in the amount of tin in different samples is an important point that is well evident in the bronze pieces of Jeyrān Tepe. This difference could be due to the use of uncontrollable methods in the production of bronze. In fact, ancient metalworkers could not mix a certain amount of copper and tin in each alloying process and produce the same alloy every time [27-32]. According to the above, it can be stated certainly Ozbaki metalworkers were familiar with the bronze alloy and they combined copper with tin for its improvement, which increased the hardness of the pieces [33]. After copper and tin, oxygen, carbon and silicon are the most frequent elements, respectively. An element like chlorine may be related to the corrosion process, which was only observed in a small amount in one sample. Oxygen has been observed frequently in the samples, the corrosion process continues with the reaction between chlorine and the remaining metallic copper intensifies this with the formation of copper chloride and the presence of oxygen [34-35]. In addition, elements such as strontium, magnesium, aluminum and silicon can be related to the samples buried in the soil for a long time.

The difference in the amount of tin in prehistoric bronze pieces in Iran is common and in many analyzes of bronze pieces [36-38]. In some mentioned references, the variety of composition in prehistoric bronze alloys was due to the different functions of different pieces. According to the literature review in Mesopotamia, metalworkers of ancient times used specific ratios of tin to copper such as 9:1, 8:1 or 16:1 to make various pieces [39]. But the studies on bronze pieces in the Iron Age of Iran have shown that such ratios were not used [40-38]. What can be said about the production of these pieces is that copper and tin were used in the construction of bronze objects. As stated by Chase, pure copper caused problems due to its high melting point and the absorption of various gases, especially oxygen during casting [41-42]. Therefore, adding tin not only causes lowering the melting point, but also as a regenerator prevents porosity [9]. To identify the general composition and the body of the pieces, the internal inclusion and corrosion layers of Sample 2 were analyzed using SEM (Table 2).

Table 2. Results of SEM-EDS Analysis of both internal and external surfaces of Sample 2

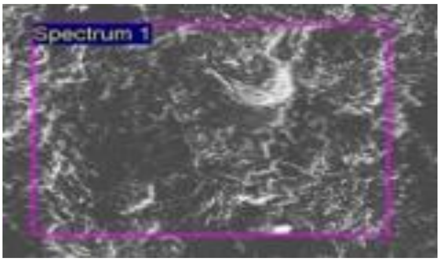
No.	Cu	Sn	O	Si	Al	Mg	Cl	C	Sr
No. 2 Section 1 (A)	69.21	-	13.94	-	1.12	-	-	15.73	-
No. 2 Section 1 (B)	84.48	-	13.92	-	1.60	-	-	-	-
No. 2 Section 2 (A)	63.14	2.29	16.59	-	-	-	-	17.00	-
No. 2 Section 2 (B)	65.85	1.22	16.54	-	-	-	-	17.38	-

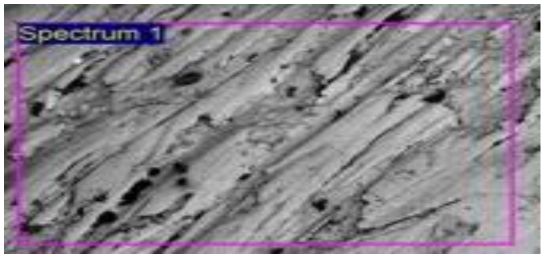
The analysis results showed that the average copper in Area 1 is 66.17% and 16.75% in Area 2, and tin was only observed in a small amount in Area 2. As shown in Table 2, after copper, oxygen and carbon are the most frequnet elements, and aluminum is observed in a small amount, which may be related to the samples buried in the soil for a long time. In corrosion layers on pieces, the amount of copper in the inner layer is higher than the outer layer, which means that the inner layers are rich in copper. The studied works have very little corrosion and the corrosion layers in these pieces are not thick. According to the analysis in this study, it can be stated that the absence of sulphide and lead particles in the samples was due to the extraction of copper from oxide ore and the production of pieces from copper oxide (Cu_2O) [43-44]. Inclusion is actually caused by the reaction of molten metal with materials used for the extraction process and / or oxygen in the melt or air, including copper oxide [45-35]. Based on the results of XRD analysis, the composition of the inclusions in the samples includes copper oxide (Cu_2O) and we can say that the inclusions are oxides and composed of cuprite (Cu_2O) (Table 3).

Table 3. Results of XRD Analysis of Metal Inclusion in Jeyrān Tepe

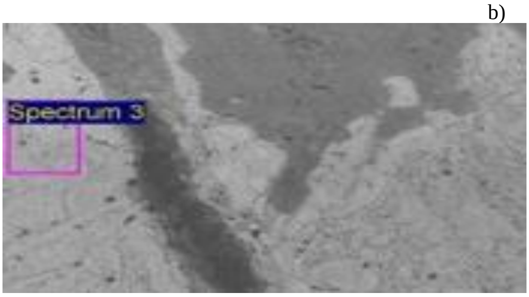
Sample	Composition	Formula	Ore
1	copper-cuprite	Cu_2O	oxide
2	copper-cuprite	Cu_2O	oxide
3	copper-cuprite	Cu_2O	oxide
4	copper-cuprite	Cu_2O	oxide
5	copper-cuprite	Cu_2O	oxide

Therefore, it can be said that the chemical composition of inclusion samples showed copper oxide (cuprite), the temperature required for its melting is between 900 °C and 1100 °C. But what is important in metallographic studies, regardless of the composition of inclusion, is their shape. According to the microscopic images, the existing inclusions are flat and elongated (Fig. 5.a) and we can also see the porosity (Fig. 5.b), which indicates that they were made by casting and malleable. To identify the operations performed for shaping the pieces, based on the metallurgical microscope images, it can be stated that the microstructure consisted of deformed coaxial grains of alpha solid solution type with twin lines inside the grains (Fig. 5.c). Metals such as copper (solid solution of alpha phase in copper and tin) is recrystallized by twinning process.





a) b)



c)

Fig. 5. SEM-EDS Microscopic Images of the Etched Cross-Section of Bracelet and Hairpin at 200 × Magnification: a) figure showing elongation; b) zone with porosity; c) grains microstructure

New crystals that arise after annealing the deformed parts are of copper alloys and cause an effect like a mirror reflection plane in the crystal, which causes smooth and parallel lines in some or all crystals. The smooth twin lines indicate that annealing was the final operation for shaping the piece, but the presence of existing twin and strain lines inside the grains indicate that the final operation included cold work on the piece.

Conclusions

In this study, 5 metal pieces related to the Iron Age of Jeyrān Tepe in the central plateau of Iran were studied to identify the type of alloy used for the production of pieces and the elemental composition of the samples in terms of major and minor elements in this field. The results showed that the samples can be divided into two general categories: samples that are made of pure copper and samples that are made of a combination of copper and tin and another element as an alloying material was not added to the mix intentionally. The amount of copper in copper pieces is between 34.25 and 84.48%. In metals from bronze alloy, the amount of tin varied between 6.46 and 14.73%. The amount of copper in these samples varied between 25.34 and 74.11%. This does not show the same pattern. According to the results of the tests, it can be said that they used uncontrolled alloying method to produce bronze pieces in Jeyrān Tepe**.** The production of bronze alloy with various amounts of tin has also been observed in the north, northwest and west of Iran. The presence of other elements in the composition of the samples, including strontium, magnesium, aluminum and silicon, shows that these elements were not intentionally added to the composition of the alloy, but are only impurity added during the process of extracting the primary ore to reach the metal.

Acknowledgments

The authors are grateful Mrs. Sadeghi in charge of SEM-EDS, XRD to the laboratory of Ferdowsi University, Mashhad and Dr. Yousefi Zoshk for providing the samples.

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Received: May 10, 2022
Accepted: June 15, 2022