Preliminary Metallurgical Investigation of Copper-Based Artifacts at Tepe Sagzabad in Qazvin Plain, Iran (1500-800 BC)

Mohammad Mortazavi [1,*], Ahmad Salehi Kakhki [1], Mohammad Ali Golozar [2], Hassan Tala'i [3]

[1] *Faculty of Conservation, Art University of Isfahan, Isfahan, Iran*

[2] *Department of Materials Engineering, Isfahan University of Technology, Isfahan, Iran*

[3] *Department of Archaeology, University of Tehran, Tehran, Iran*

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Tepe Sagzabad, a site situated on the Qazvin Plain of north-central Iran, was excavated from 1970 to 1998 by the Institute of Archaeology of Tehran University. Recent excavations by H. Tala'i (1997-1999) yielded some metal artifacts dating to the Early Iron Age. Ten of these copper-based samples were investigated using inductively coupled plasma optical emission spectroscopy (ICP-OES), scanning electron microscopy combined with energy dispersive X-ray spectroscopy (SEM-EDX) and optical microscopy (OM). The results of these analyses showed that the metal objects at Tepe Sagzabad are made of different copper alloys, including: pure copper, copper-arsenic and copper-tin. In addition, multiple procedures, including hot-working, cold-working, and annealing were used as manufacturing techniques. The copper-based objects from Tepe Sagzabad provide evidence for the continued use of pure copper and arsenical copper alongside tin bronzes on the Iranian Plateau during the Early Iron Age.

Keywords: *Sagzabad, Qazvin Plain, Iranian Plateau, Archaeometallurgy, Copper alloys, Iron Age*

Introduction

Archaeological evidences emphasizes Iranian Plateau, rich in raw material, as one of the origins of metallurgy occured in Southwest Asia (Pigott 2004a: 28). In particular, the Qazvin plain in the northwestern part of the Central Plateau of Iran is known for its prehistoric metallurgical finds (fig.1). Three major prehistoric sites lie on the plain: Zagheh, Ghabristan and Sagzabad. Together, they comprise a settlement sequence extending from the Early Chalcolithic to the Iron Age (Negahban 1976, Tala'i 2002). Metal objects, moulds, crucibles, and well-preserved metallurgical workshops from Tepe Ghabristan (Late Chalcolithic, or 4th millennium BC) show that this area was one of the earliest copper smelting regions in the Iranian Plateau, and by extension, in all of Southwest Asia (Thornton 2009: 312, Pigott 2004a: 37, Pigott 1999: 77).

Settlement on the Qazvin Plain continued to the Late Bronze age and through to the Iron Age at Tepe Sagzabad, a site located 300 m east of Tepe Ghabristan (Tala'i 1984). A variety of metal objects such as rings, buttons, arrowheads, mace heads, plaques, pendants and a saw have been found during the eleven seasons of excavation at Sagzabad from 1970 to 1999 (Tala'i 1984, Malek Shahmirzadi 1979). The assemblage of metal tools from Sagzabad comprises one of the most significant samples for archaeometallurgical studies of the Iron Age on the Iranian Plateau.

The Central Plateau of Iran is also rich in metal deposits (Rousta'i 2004: 222, Pigott 1999). In addition, a stretch of the Silk Road passed through the Qazvin Plain, and from there continued westward to Azerbaijan (Malek Shahmirzadi 1979: 50). Therefore, based upon archaeological evidence and its geographic location, this area could have been one of the centers for export and import of metal goods and raw materials in antiquity.

Accordingly, this research is concerned with metallurgical examination of a sample of copper-based artifacts found in the most recent excavations at Sagzabad in 1997-1999 that dated to the Iron I and II Periods (1500-800 BC),(Tala'i 2002).

*Corresponding author. E-mail address: m.mortazavy@aui.ac.ir

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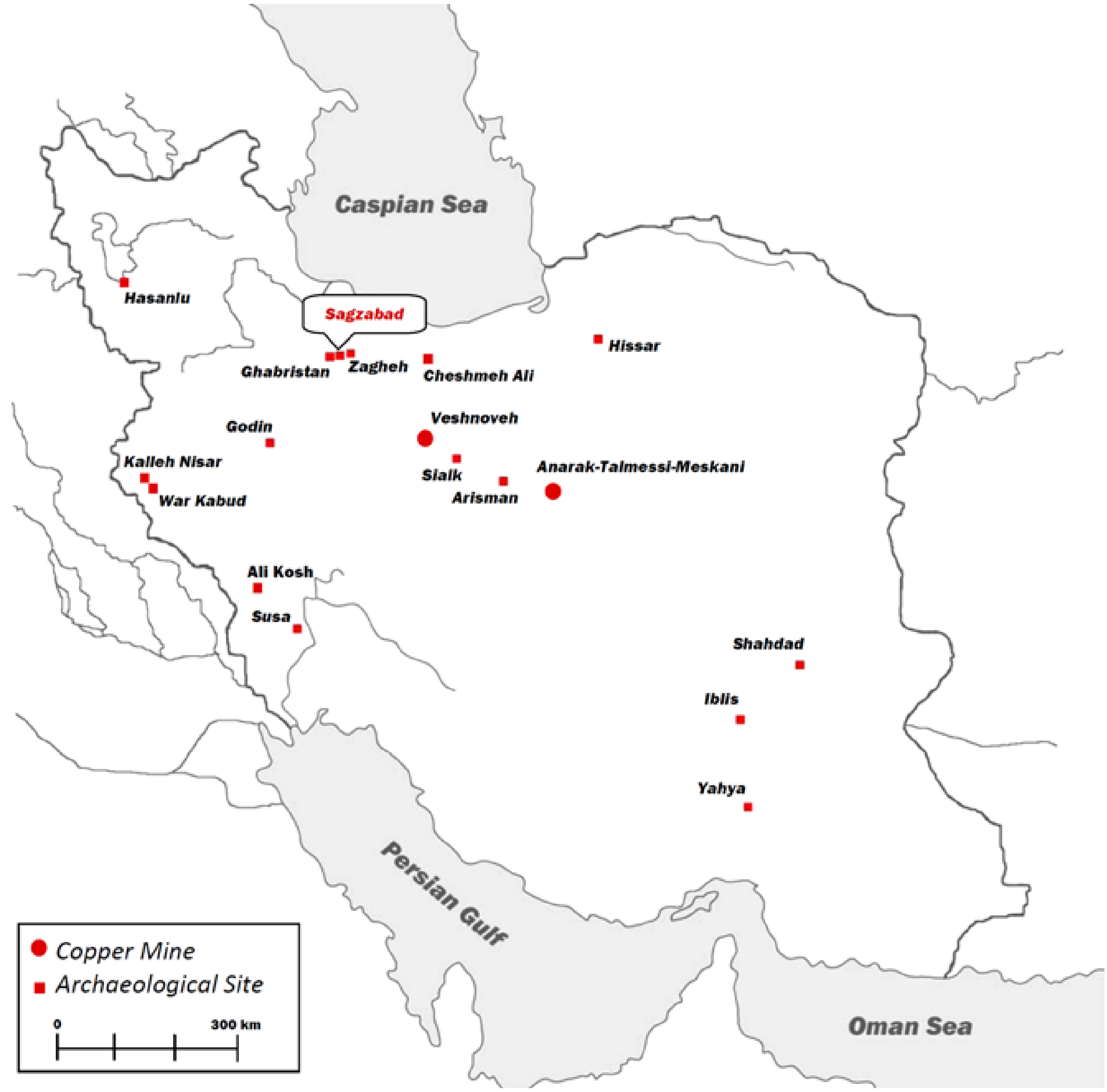


Fig. 1: *Map of archaeological sites in Iran showing the location of Tepe Sagzabad.*

Tepe Sagzabad

Tepe Sagzabad is later than Zagheh and Ghabristan chronologically, dating to the Late Bronze through Iron Ages. The mound extends approximately 350 meters from north to south and approximately 400 meters east to west (Negahban 1976: 249, Malek Shahmirzadi 1979: 50). The first excavations at Tepe Sagzabad were part of a project undertaken by Department of Archaeology and the History of Art and the Institute of Archaeology of Tehran University in the Qazvin Plain, which began in 1970 and continued to 1977 (Malek Shahmirzadi 1979, Tala'i 1984). After a hiatus of twenty years, excavation was resumed by H. Tala'i from 1997 to 1999. His work yielded metal artifacts dating back to the Iron Age (Tala'i 1984). Tepe Sagzabad consists of 10 meters of archaeological deposits, of which only five meters stand higher than the level of surrounding plain (Malek Shahmirzadi 1979) (fig.2). The site itself is located along the major East-West trade route. Connecting the northern part to the southern part of the Iranian Plateau.

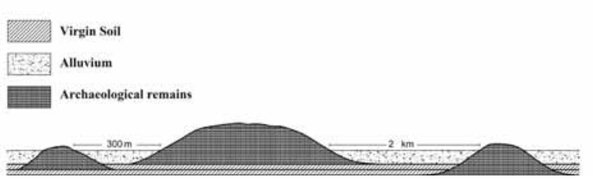


Fig. 2: *Sketch map of sits of Ghabristan, Sagzabad and Zagheh (from left) (After: Negahban 1976)*

Sampling

Ten pieces of copper-based samples, which were found during the 1997-1999 excavations at Tepe Sagzabad, were selected for investigation (Table. 1 for details on the contexts of each sample). These samples originated from the stratified Iron I and II settlement site (1500-800 BC) (Tala'i 1983). Six pins, two thin sheet fragments, one small thin sheet tube, and one arrowhead were examined. Unfortunately, the tube was heavily corroded and no sound metal remained in it.

Sample No.	Description	Excavation Characteristics
Sg76-1	Thin sheet fragment	Tr. 400
		L. 411
Sg76-2	Pin	Tr. 600
		L. 602
Sg76-3	Pin	Tr. 200
		L. 203
Sg76-4	Pin	Tr. 700
		L. 704
Sg76-5	Pin	Tr. 200
		L. 203
Sg76-6	Pin	Tr. ---
		L. ---
Sg76-7	Pin	Tr. 600
		L. 605
Sg76-8	Small thin sheet tube	Tr. 700
		L. 706
Sg78-9	Pin	Tr. 1900
		L. 1905
Sg76-10	Thin sheet fragment	Tr. Surface
		L. Surface

Table 1: *Metal Finds from the Tepe Sagzabad excavation that are included in this study.*

Methods of Analysis

All of the samples were thoroughly examined in order to find exact details of the chemical compositions and the manufacturing techniques. In order to study the chemical composition, inclusions and microstructures, three complementary analytical methods were used: inductively coupled plasma optical emission spectroscopy (ICP-OES), scanning electron microscopy combined with energy dispersive X-ray spectroscopy (SEM-EDX), and optical microscopy (OM).

ICP-OES Variant 735 was used to determine the chemical composition of samples. Samples for ICP-OES analysis (about 0.5 g) were cut using a jeweler's saw. Great care was taken to clean the core metal from the surface corrosion products.

Longitudinal sections of samples were also taken with jeweler's saw. The samples were embedded in Buehler epoxy resin and polished using silicon carbide abrasive paper (up to 1200 grit). In the case of samples Sg76-2, Sg76-5 and Sg76-8 with deep penetrated corrosion, EDX analysis on large areas of the polished section was used to obtain representative average values of alloy composition. SEM-EDX analysis was also used to determine the composition and morphology of inclusions in the microstructures. SEM-EDX analyses were carried out using the VEGA II TESCAN, Czech Republic. EDX: Rontec, Quantax/QX2, Germany in Razi Metallurgical Research Center, Tehran, Iran.

Samples for metallographic study were polished with diamond paste down to 0.25 µm. The polished sections of the samples were etched using an aqueous ferric chloride solution (10 g $FeCl_3$+ 30 ml HCl+ 120 ml H_2O). The microstructures were examined using a BK-POL/BK-POLR optical microscope equipped with a Canon EOS Kiss X4 CCD camera and Breeze System image capture software. The aim of metallographic examination by optical microscopy (OM) was to study the microstructures to provide information on the techniques employed in manufacturing.

Results

Chemical Composition Analysis by ICP-OES and SEM-EDX

The result obtained from ICP-OES analyses (wt%) are presented in Table. 2. Seven metal artifacts, including two thin sheet fragments and five pins, were analyzed. From the results obtained, three main groups can be distinguished: unalloyed copper, copper alloyed with arsenic, and tin bronze. One sheet fragment (Sg76-10) and two pins (Sg76-4 and Sg76-7) were made from unalloyed copper. Sheet fragment Sg76-1 was made from arsenic-copper alloy and pins Sg76-3, Sg76-6 and Sg78-9 were made from tin bronze. ICP analyses also revealed Lead, P, Zinc, Nickel, Iron and Silver as minor alloying elements.

Three metal artifacts including a thin sheet tube, a pin, and an arrowhead were analyzed by EDX. EDX analyses of samples Sg76-2, Sg76-5 and Sg76-8 revealed the following results (Table. 3). The thin sheet tube (Sg76-8) was completely mineralized in such a way that the original shape can be seen. The tube was found to be a tin bronze, containing 8wt%Sn in the mineralized structure. However, the analysis showed high amount of chlorine (32wt%Cl), a result probably due to corrosion processes. EDX analysis of the metallic cores belong to Sg76-2 and Sg76-5 indicated that these samples are composed of unalloyed copper and low tin bronze respectively.

Sample Number	Object	Cu	As	Sn	Ag	Fe	Ni	Pb	Zn	P	Si	Total
Sg76-1	Sheet fragment	94.58	4.19	0.00	0.01	0.16	0.01	0.22	0.33	0.51	0.00	**100.01**
Sg76-3	pin	87.88	0.12	6.63	0.03	0.20	0.00	0.14	0.31	0.49	3.84	**99.64**
Sg76-4	pin	98.67	0.24	0.01	0.02	0.12	0.02	0.03	0.35	0.52	0.00	**99.98**
Sg76-6	pin	90.83	0.02	4.76	0.08	0.15	0.18	0.17	0.29	0.42	2.99	**99.89**
Sg76-7	pin	99.30	0.06	0.00	0.02	0.00	0.00	0.00	0.35	0.48	0.00	**100.21**
Sg78-9	pin	91.83	0.02	4.26	0.07	0.15	0.17	0.18	0.28	0.43	2.90	**100.29**
Sg76-10	Sheet fragment	98.20	0.17	0.00	0.12	0.15	0.00	0.01	0.33	0.81	0.00	**99.79**

Table. 2: *Elemental composition (wt%) of the Tepe Sagzabad fragments determined by ICP-OES .*

Sample Number	Object	Cu	As	Sn	Ag	Fe	Ni	Pb	Zn	P	Si	Bi	S	Cl	Total
Sg76-2	arrowhead	98.5	0.0	0.1	0.0	0.2	-	0.0	0.0	-	-	0.4	0.7	-	**99.9**
Sg76-5	Pin	94.7	0.8	2.0	-	0.8	-	0.4	1.3	-	-	0.0	0.3	-	**100.3**
Sg76-8	Sheet tube	58.2	0.1	8.2	-	0.3	-	0.0	0.0	-	-	0.0	0.7	32.6	**100.1**
Sg76-3	Pin	91.5	0	7.2	-	0.8	-	0.6	-	-	-	0	-	-	**100.1**
Sg76-6	Pin	93.7	0	5.9	-	0	-	0	0	-	-	0.2	0.8	-	**100.6**
Sg78-9	Pin	90.2	0	7.3	-	0.2	-	0	0.4	-	-	0.5	0.7	0.8	**100.1**

Table 3*: Elemental composition (wt%) of some fragments from Tepe Sagzabad determined by EDX analyses.*

SEM-EDX analysis was also used to determine the chemical composition of inclusions. Results obtained (Table. 4) showed that they mainly consisted of copper, iron and sulfide.

Sample Number	Fe	Cu	Sn	Pb	S	Total
Sg76-1	1.4	84.2	-	-	14.4	**100.0**
Sg76-2	0.2	89.8	-	-	10.1	**100.1**
Sg76-4	0.4	79.7	-	-	19.9	**100**
Sg76-5	2.3	76.2	-	-	21.5	**100**
Sg76-6	0.0	79.9	-	-	20.1	**100**
Sg78-9	0.0	76.5	0.8	-	22.7	**100**
Sg76-10	2.1	77.4	-	0.5	20.0	**100**

Table 4: *Elemental composition (wt%) of inclusions detemined by EDX analyses*

Microstructural Investigation

All samples, except the thin sheet tube, were examined to reveal their microstructures using optical microscope and SEM. Metallographic examination of samples showed as-worked structures. The microstructures of the metal objects revealed recrystallized twin grain structures (figs. 3, 4, 5) for pins (Sg76-3, Sg76-5, Sg76-6, and Sg78-9) and sheet fragment (Sg76-10). Presence of blue-grey elongated sulfide inclusions along the longitudinal section of samples (figs. 3, 5, 6) implies metalworking (hammering) to achieve the desired shape. Presence of annealing twins indicates that these artifacts were annealed after or during working process (Frame 2010: 1705).

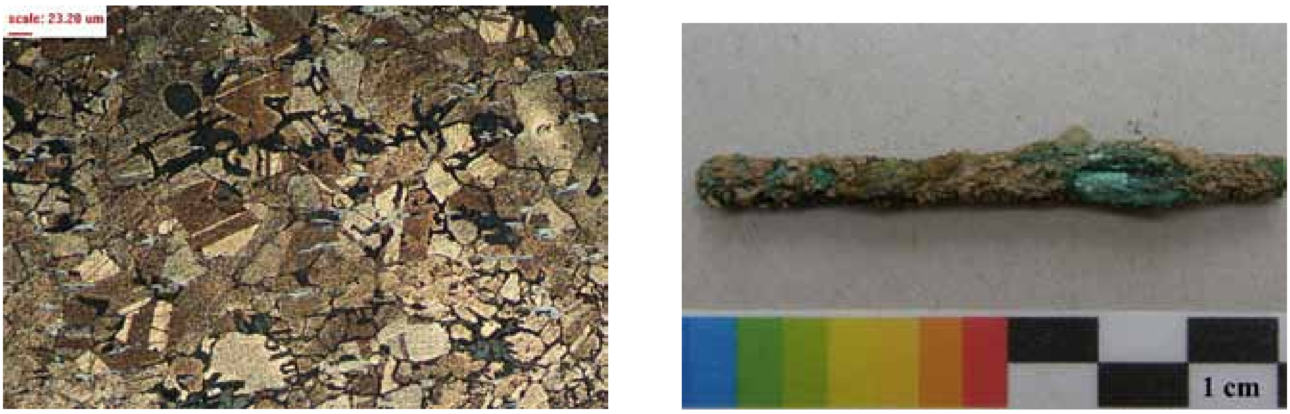


Fig. 3: *Pin, Sg76-6.* ***Left:*** *Longitudinal section, OM image of the etched sample showing recrystallized twin grain structure with blue-grey elongated sulfide inclusions.* ***Right:*** *Full fragment. (Etchant: aqueous ferric chloride)*

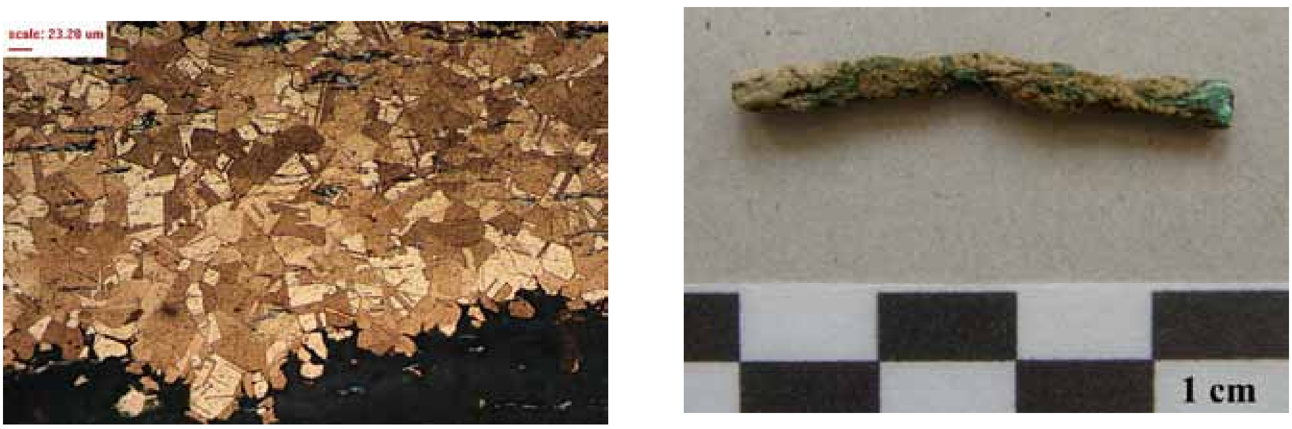


Fig. 4: *Pin, Sg76-5.* ***Left:*** *Longitudinal section, OM image of the etched sample showing recrystallized twin grain structure with blue-grey elongated sulfide inclusions.* ***Right:*** *Full fragment. (Etchant: aqueous ferric chloride)*

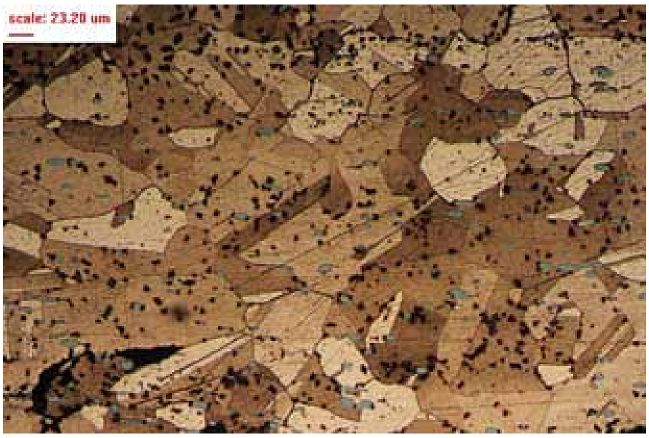
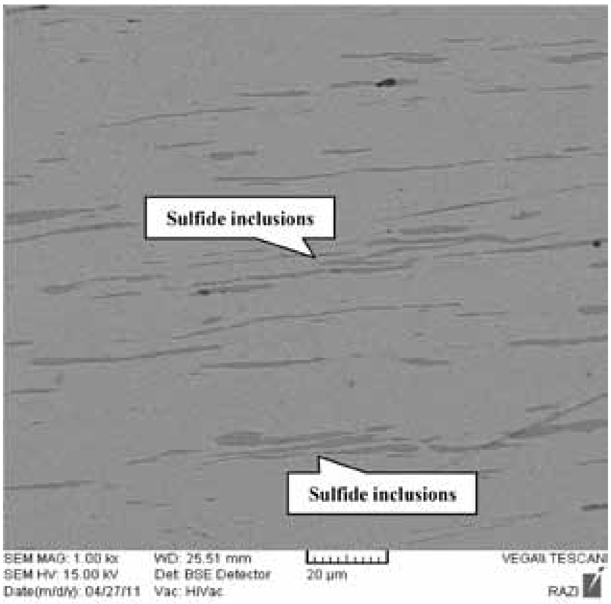


Fig. 5: *Sheet fragment, Sg76-10.* ***Left:*** *Longitudinal section, OM image of the etched sample showing recrystallized twin grain structure with blue-grey elongated sulfide inclusions.* ***Right:*** *Full fragment. (Etchant: aqueous ferric chloride)*



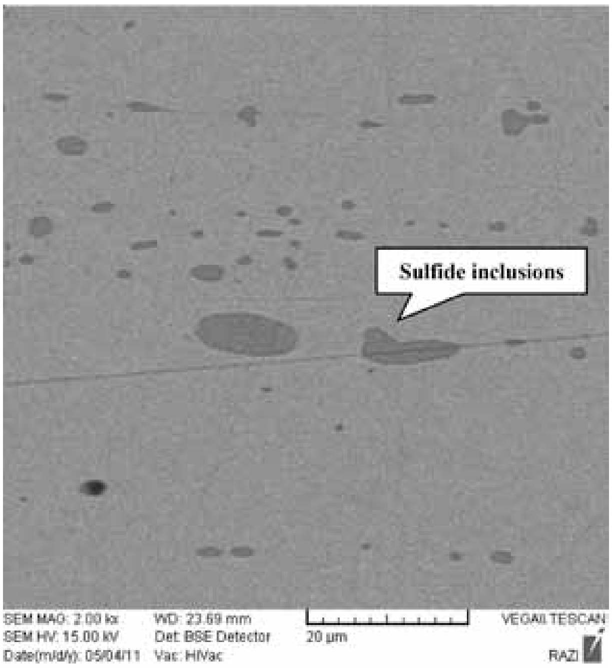


Fig. 6: ***Left:*** *Longitudinal section, BSE image of the unetched sample No.Sg76-4 (Pin) showing heavily elongated inclusions along the longitudinal section of the pin.* ***Right:*** *Longitudinal section, BSE image of the unetched sample No.Sg76-10 (Sheet fragment) showing elongated inclusions along the longitudinal section.*

The arrowhead (Sg76-2) and one pin (Sg76-7) showed worked deformed grains revealing some distorted twins (fig. 7), which are signs of working after the final annealing (Scott 1991: 91). The sheet fragment, Sg76-1, shows a typical recrystallized and heavily worked structure. Many fine slip lines and strained grains are the result of additional metal forming such as hammering after multiple procedures, including hot-working or cold-working, and annealing to shape the sheet (Scott 1991: 113).

Fig. 7: *Pin, Sg76-7.* ***Left:*** *Longitudinal section, OM image of the etched sample showing worked deformed grains and distorted twin bands.* ***Right:*** *Full fragment. (Etchant: aqueous ferric chloride)*

Although it was difficult to see the microstructure of the pin (Sg76-4) as a result of its very fine grain size, SEM and OM images clearly showed heavily elongated inclusions along the longitudinal section of the pin (fig. 6). These deformed inclusions can be an indication of heavy hot/cold working (Frame 2010: 1705).

Discussion

Results obtained from ICP and EDX analyses of the copper-based objects from Tepe Sagzabad showed different elemental compositions. Relatively pure copper, arsenical copper and tin bronzes were found to be used in the Iron I and II settlement (1500-800 BC) simultaneously (fig. 8). The microstructures of the samples showed the effects of heavily worked and fully annealed grains. All the fragments contained sulfur compound inclusions (Cu-Fe-S) elongated along the length of the objects, indicating the effects of heavy hot/cold working to achieve the final shape (Frame 2010: 1707, Scott 1991, Artioli 2010). Despite the variety of macro-composition, it is noteworthy that minor elements such as Nickel, Lead, Silver, Arsenic, Zinc, and Iron were present in all of the samples.

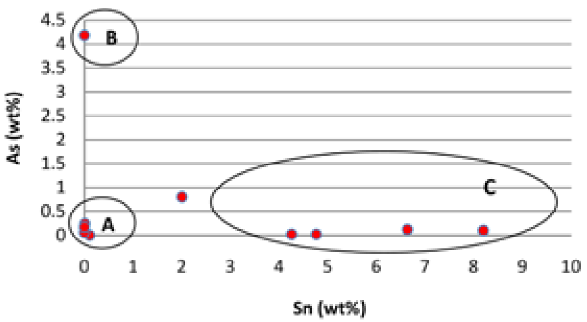


Fig. 8: *Scatter plot of the arsenic vs. tin content measured by ICP and SEM-EDX for the Tepe Sagzabad samples:* ***(A)*** *low-impurity copper,* **(B)** *arsenical copper,* **(C)** *tin bronze.*

As stated minor elements are common impurities found in ancient copper artifacts that occur as a result of the smelting process (Artioli 2010: 310; Chiavari et al. 2011). Elements similar to those identified in these copper-based objects have often been reported on different parts of Iranian Plateau such as in Luristan (Fleming et al. 2006, Fleming et al. 2005, Begemann 2008), at Godin Tepe (Frame 2010), Tepe Yahya (Thornton et al. 2002) and Tepe Sialk (Nezafati et al, 2008). Nevertheless, there are obvious differences in all the samples containing substantial amounts of phosphorus. In addition, it is interesting to note the presence of high amounts of silicon (c. 3wt%Si) in the tin bronze group.

Unalloyed Copper

Despite differences in shape, the artifacts in this group were all made from unalloyed copper. Relatively pure copper ranging from 98wt%-99wt%Cu was observed in two pins (Sg76-4 and Sg76-7), the sheet fragment (Sg76-10) and the arrowhead (Sg76-2). Although these samples contained small amount of arsenic (< 0.3wt%As), it is unlikely to be due to deliberate alloying (cf. Lechtman 1996: 509). On the other hand, levels of tin were extremely low (< 0.1wt%Sn) in all these samples.

Although arsenic-copper alloy appeared in the Iranian Plateau by the end of fifth millennium BC (Thornton & Lamberg-Karlovsky 2004, Pigott 2004a, Thornton et al. 2002) and gradually replaced pure native copper, such changes did not take place simultaneously in all over the Iranian Plateau. Despite decrease of the use of pure copper after the invention of smelting and alloying arsenical copper, the use of unalloyed copper continued into the Bronze Age (Frame 2010, Thornton et al. 2002). Frame (2010) identified an arrowhead which was made of almost pure copper (99.95wt%Cu) from Godin Tepe, Period III:2 (1900-1600 BC). Analyses by Thornton et al. (2002) showed that pure copper has been used to make some artifacts from Tepe Yahya, Period IVB. The use of unalloyed copper in the Bronze Age may be for aesthetic properties, as cited by Hosler (Thornton & Lamberg-Karlovsky 2004: 267).

Nonetheless, investigations of the Iron Age metal artifacts from Godin Tepe (Frame 2010), Luristan (Fleming et al 2005), Tepe Yahya (Thornton et al. 2002) and Hasanlu (Pigott 2004b) have demonstrated that the use of pure copper has disappeared in this period. In this case, limited objects are presented; in fact, samples from Sagzabad show predominant use of almost pure copper even in the Iron Age. During the Iron Age, the use of copper alloy continued for ornaments and decorative items (Pigott 2004b, Frame 2010, Fleming et al. 2006). Accordingly, the two copper pins studied in this work (Sg76-4 and Sg76-7) may be classified as decorative items which were made of pure copper for desired color. As thin sheet fragment (Sg76-10) was very small, it is very difficult to suggest any concept. But as its recrystallized twin grain structure revealed, it might have been part of a copper artifact which has been worked and annealed to achieve the require shape. Regarding the arrowhead (Sg76-2) some questions should be answered. Unalloyed copper is soft and not suitable for which implement probably was used. On the other hand, its worked deformed grain structure is incomparable with the large annealed structure which is highly desirable for the high-toughness (Fram 2010:1708).

Arsenical Copper Alloy

The thin sheet fragment, Sg76-1, can be defined as an arsenical copper alloy. Appreciable amount of arsenic (c. 4wt%As) was detected in the chemical composition of the fragment. This amount suggests that the arsenic-copper alloy could be an intentional product (Lechtman 1996: 509, Junk 2003: 5). 4wt% arsenic is below the solid solubility limit of arsenic in copper, which produces an α solid solution with good strength and ductility (Lechtman 1996: 482, Junk 2003: 24, Moorey 1969: 133). The structure of Sg76-1 contains elongated inclusions and slip lines across the longitudinal section, indicating a worked structure.

Although, arsenical copper alloys were used in fifth millennium BC on the Iranian Plateau, it was the most common alloy until the Iron Age (Thornton et al 2002: 1452). Metallurgical investigations of Iron Age finds from Tepe Yahya (Thornton et al. 2002), Godin Tepe (Frame 2010), Dailaman and Marlik (Pigott 1999: 91) have shown that arsenical copper continued to be produced in this period, but tin bronzes were predominant. Analyses of excavated copper-based artifacts from three Iron Age sites in Luristan - Bard-i Bal, Kutal-i Gugul, and War Kabud – have shown that by the Iron Age, arsenic is no longer an important alloying element (Fleming et al 2005). On the other hand, decrease in the use of arsenical copper corresponds to what we expected when only one sample was identified in Iron Age samples from Sagzabad.

Tin Bronze

Five samples identified as tin bronze (Cu-Sn) artifacts displayed a wide variety of tin content ranging from 2wt% to 8wt%. The three pins, Sg76-3, Sg76-6 and Sg78-9, which were analyzed by ICP-OES showed high amounts of tin (c. 4wt%-6wt%Sn). EDX Analysis of a pin (Sg76-5) revealed low level of tin (2wt%Sn), which suggests the use of tin bronze alloy. The thin sheet tube (Sg76-8) was also analyzed by SEM-EDX, which showed a high amount of tin (8wt%Sn). Sg76-8 was completely mineralized, and therefore the high tin content of this sample does not reflect the accurate chemical composition. Copper-tin alloys containing less than

17wt%Sn can be cold-worked and annealed (Scott 1991: 26).

Perhaps on this basis, prehistoric metallurgists eventually aimed at an alloy near 10wt% tin (Coghlan 1975: 35, Moorey 1969: 135, Park et al. 2009: 1268). It is interesting to note that all the samples had elongated inclusions and recrystallized twin grain structures representative of hammering and annealing. Equiaxed grains with straight twin bands are evidence of annealing as a final treatment. It must be mentioned that due to heavy corrosion effects, the microstructure of the sheet tube was impossible to discern.

Although copper-tin alloys first appeared during the early third millennium BC in the Iranian Plateau (Frame 2010: 1705), it was at the end of the Late Bronze Age which the tin bronze mostly replaced the arsenic alloys (Eaton & Mckerrell 1976: 147, Lechtman & Klein 1999: 497). By the Iron Age, although iron was the material of choice for tools and weapons, the popularity of tin bronzes did not decrease. Tin bronze continued to be used for certain weapons, jewelry items, personal ornaments, and equestrian gear (Pigott 2004b: 350, Pigott 1999: 91, Fleming et al. 2005). Analyses of Iron Age copper-based metal artifacts from Luristan (Fleming et al. 2005) showed the use of tin bronze to be prevalent. Studies by Thornton et al. (2002) revealed two pins from Tepe Yahya, Period II, made of true tin bronze alloys (4wt%Sn and 9.8wt%Sn). Analyses of metal artifacts from Godin Tepe Period II by Frame (2010) showed a pin and a bracelet made from tin bronzes. The Iron Age pins recovered from Tepe Sagzabad are made of tin bronze, corresponding with other Iron Age sites on the Iranian Plateau.

The most notable exception for tin bronze samples from Sagzabad is the presence of high amounts of silicon (c. 3wt%Si) in the following three pins, Sg76-3, Sg76-6 and Sg78-9 (Table. 2). Such high levels of silicon in tin bronze have not been reported by other scholars for copper-based artifacts. Similar to other ICP analysis, all samples were cleaned completely, to make sure to eliminate all contaminations. Thus, the high level of silicon content could not be due to corrosion. High values of silicon in these samples could not be explained from archaeometallurgical viewpoint. On the other hand, Si was not detected in EDX analysis of samples Sg76-3, Sg76-6, Sg78-9 and also Sg76-2, and Sg76-8 (Table. 3). Hence, it may actually be a result of spectral overlap or other instrumental factors rather than a reality of the metals themselves. It is believed that the thin sheet tube had been formed from a sheet of tin bronze. The tin sheet is supposed to be bent to shape the tube, as both ends overlap each other.

Conclusions

Although the group of objects analyzed was very limited, it can be concluded that the Iron Age I and II Periods (1500-800 BC) at Tepe Sagzabad witnesses the use of a wide variety of compositions in the production of copper alloys. Unalloyed copper, arsenical copper and tin bronzes were identified in this region. This diversity of alloy composition is meaningful with regard to the location of Sagzabad along the trade routes and its interaction with other ancient civilizations. Unfortunately, however, it is difficult to determine where these objects were manufactured, in terms of weather they were recovered in situ or whether they were imported.

The variety of copper alloys in Tepe Sagzabad is similar to results obtained by Frame (2010) from Godin Tepe, Period II. The location of these sites along the trade routes could be a subject of further investigation regarding cultural impacts of civilizations. This is especially meaningful, as some tin bronzes in Tepe Sagzabad were identified while transition of tin from sources in Afghanistan across the Iranian Plateau and into Mesopotamia was debatable (Pigott 2004a, Frame 2010).

All the samples, except the sheeted ones, can be classify as decorative objects, apparently showing that the copper alloys were alloys of choice for decorative items in Iron Age. On the other hand, the variety of alloys can be an indication of deliberate alloying which may suggest a significant aesthetic value for different alloys. This is apparent from the amounts of tin and arsenic in composition. Despite differences in composition, it is noteworthy that all the specimens were made by either hot working, or cold working followed by annealing.

In addition, the relatively impurity-free nature of alloys reflects the improved smelting and refining technique. The presence of minor elements is a likely indicator of the use of copper ores with corresponding impurities; similarity in minor elements in all the samples could also be an evidence of some relations between the objects. According to analogy of trace elements in unalloyed copper, arsenical copper and tin bronzes may imply direct addition of these metals to create copper-base alloys noted by Thornton et al. (2002: 1451) and Coghlan (1975: 35).

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