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Metallography and microstructure interpretation of some archaeological tin bronze vessels from Iran

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ABSTRACT

Archaeological excavations in western Iran have recently revealed a significant Luristan Bronzes collection from Sangtarashan archaeological site. The site and its bronze collection are dated to Iron Age II/III of western Iran (10th–7th century BC) according to archaeological research. Alloy composition, microstructure and manufacturing technique of some sheet metal vessels are determined to reveal metallurgical processes in western Iran in the first millennium BC. Experimental analyses were carried out using Scanning Electron Microscopy–Energy Dispersive X-ray Spectroscopy and Optical Microscopy/Metallography methods. The results allowed reconstructing the manufacturing process of bronze vessels in Luristan. It proved that the samples have been manufactured with a binary copper–tin alloy with a variable tin content that may relates to the application of an uncontrolled procedure to make bronze alloy (e.g. co-smelting or cementation). The presence of elongated copper sulphide inclusions showed probable use of copper sulphide ores for metal production and smelting. Based on metallographic studies, a cycle of cold working and annealing was used to shape the bronze vessels.

1. Introduction

The investigation of microstructure and alloy composition of archaeological metal artefacts is an interesting and important subject to determine metalworking techniques in the ancient world. Tin bronze is the first alloy used in most regions around the world, for example, the first tin bronze artefacts appear in west of Iranian Plateau at the end of Chalcolithic period (end of 4th millennium BC) [1–3].

The Luristan region is located in the west of Iran, which is one of the important cradles of the Iranian Plateau. In archaeological context, Luristan is the highland folded region in the Central Zagros mountain chain, in western Iran. Thousands of ancient bronze artefacts with exquisite modelling, fine style, and outstanding manufacturing skill have been unearthed in the Luristan area. The emergence of significant bronze production is an important archaeological/technological phenomenon during the Iron Age in the Luristan region. The Luristan Bronzes include a series of decorated bronze artefacts similar in specific local style, dating to the Iron Age II/III (1000–650 BC) [4–10]. During the past 10 years, some archaeological excavations were carried out in Iron Age site of Sangtarashan in eastern Luristan (known as Pish-i Kuh). Sangtarashan is situated about 35 km of southeast of Khorramabad (capital of Lorestan province). The site has been excavated by Iranian archaeologists, Ata Hassanpour and Mehrdad Malekzadeh. Archaeological evidence proves that the site contains the remains of an Iron Age II sanctuary with stony architecture. Also about 2000 bronze artefacts have been discovered together with some other objects such as iron, bone, stone and pottery. In fact, the majority of objects recovered from Sangtarashan are different kinds of bronzes in the Luristan Bronzes style such as spouted and simple vessels, sculptural object such as finials, and weaponry artefacts. [11].

In this paper, some recent excavated bronze artefacts belonging to the Sangtarashan archaeological site were examined to determine alloying and manufacturing characteristics and processes during the Iron Age period. The metallurgical research concerning bronze production in Sangtarashan has become a unique opportunity to understand the Iron Age bronze production in this western region of the Iranian Plateau. The study also comprises a discussion concerning the elemental and microstructural features of some bronze vessels.

2. Materials and methods

2.1. Archaeological samples

To study the microstructure and alloy composition of bronzes from the Iron Age Luristan, a collection of twenty two bronze samples was selected from the Sangtarashan archaeological site. These include broken metallic vessels that have been unearthed during archaeological excavations between 2009 and 2011 (Fig. 1). Some samples were analysed

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Fig. 1. Some broken vessels from all selected samples belonging to Sangtarashan archaeological site.

and previously published [3,11] but these were reconsidered in this study next to other samples to compare and develop statistical interpretations. In total, twenty five pieces were chosen from 22 metallic vessels including 22 pieces from the vessel bodies (Nos. ST.01-10 to ST.22-11), a piece including the spout of a vessel (ST.02-10/2) and two small pins (ST.09-10/2 and ST.10-10/2). This selection was based on the fact that some bronze vessels from Sangtarashan are made with two separate pieces such as the case with spouted vessels in which the spout is manufactured by a bronze fragment that has been joined to the body with large metal pins. Therefore, one spout and two pins from three vessels are analysed.

2.2. Experimental

Small samples from the metal artefacts and fragments were prepared and mounted for metallographic preparation. For this purpose, a cross section from each piece was prepared by embedding samples in epoxy resin. Preparation for analysis was followed by grinding them with silicon carbide papers (400–2000 grit size). Finally, the cross sections were polished with a diamond paste (1 μm).

Microstructural observations and chemical composition analysis were carried out with optical microscopy and scanning electron microscopy equipped with energy dispersive X-ray spectroscopy (SEM–EDS) methods. Cross-sections were observed with a BK-POL/BK-POLR manufactured by Alltion Company, China, under bright field (BF) illumination. Samples were observed before and after etching with alcoholic ferric chloride ($FeCl_3$) solution. Mounted cross-sections were observed in a VEGA II, TESCAN scanning electron microscope equipped with a secondary electron detector (SE) and a backscattered electron detector (BSE) with elemental analysis system (EDS) model Rontec Quantax/QX2, Germany, in SEM laboratory of Razi Metallurgical Research Center, Tehran, Iran used for semi-quantitative elemental analyses. The metallic remains in cross sections were analysed by Energy Dispersive Spectrometry (EDS) on areas of about 10000 μm^2 (about 100 × 100 μm) to detect the entire alloy composition and to avoid effects of phase concentrations in the final results.

3. Results and discussion

3.1. Alloy composition

SEM–EDS investigation was employed to determine alloy components in a semi-quantitative manner. Table 1 shows results of alloy composition in 25 samples from 22 vessels carried out by SEM–EDS method. According to Table 1 it is obvious that all twenty two vessels are made of bronze alloy. Also, it is clear that the main alloying elements of all samples are Cu and Sn whereas Pb, Zn and Ni are considered to be impurities in the alloy composition. The percent of Cu content varies from 83.81 up to 95.11 and the Sn 4.18 up to 13.36. Through these analyses one can observe that the Sn contents show different values.

Lead is detected in minor concentrations in all samples. Only in two samples, ST.13-10 and ST.15-10, it is observed in a considerable amount, over 2%. Worth mentioning is that arsenic has been detected in low amounts and as a minor component (less than 1%) in all samples, while arsenic has been detected as a significant alloying element in many Iranian prehistoric copper alloys [1].

Generally, it is evident that the samples were made of a binary copper–tin alloy, and that other elements are impurities that entered the alloy during ore smelting and were not added deliberately.

According to the results of semi-quantitative chemical analysis, it is apparent that bronze vessels are produced by Cu–Sn or tin bronze alloy with a variable tin content and some metallic impurities. The variety of Sn content proves that the bronze alloy is not made by a controlled alloying process to reach a homogenous bronze composition by adding a distinct amount of tin to copper and melting them [12,13].

Table 1
Results of SEM–EDS analysis of alloy in 25 bronze samples from Sangtarashan (wt.%).

	Cu	Sn	Pb	As	Zn	Ag	P	Ni	Fe	Sb	Si	S
ST.01-10	88.61	11.32	–	0.02	–	–	0.03	–	–	–	–	–
ST.02-10	90.79	7.75	0.61	0.03	0.01	0.67	0.14	–	–	–	–	–
ST.02-10/2	89.30	10.70	–	–	–	–	–	–	–	–	–	–
ST.03-10	86.18	9.43	0.81	0.73	1.23	0.54	0.24	0.42	0.42	–	–	–
ST.04-10	84.88	13.36	1.16	0.22	0.02	–	0.20	0.01	0.01	–	–	0.15
ST.05-10	90.40	9.51	–	0.03	0.01	–	0.03	–	0.01	–	–	–
ST.06-10	89.89	8.87	0.27	0.04	–	–	–	0.59	–	–	–	0.34
ST.07-10	87.40	9.60	1.23	0.04	0.41	0.48	0.13	0.41	0.32	–	–	–
ST.08-10	86.83	11.63	0.26	0.03	0.29	0.56	0.17	–	0.23	–	–	–
ST.09-10	83.81	12.78	0.42	0.03	1.42	0.80	0.28	–	0.39	–	–	0.07
ST.09-10/2	95.11	4.18	0.56	0.13	–	–	0.02	–	–	–	–	–
ST.10-10	90.59	8.76	0.24	0.03	0.01	0.27	0.10	–	–	–	–	–
ST.10-10/2	92.26	6.29	0.03	0.46	0.58	–	–	–	0.38	–	–	–
ST.11-10	89.27	9.78	0.22	0.21	0.01	–	0.07	–	–	0.36	0.08	–
ST.12-10	91.68	8.15	–	0.03	0.01	0.09	0.02	–	–	–	–	–
ST.13-10	85.61	11.45	2.27	0.03	0.01	0.44	0.18	–	–	–	–	–
ST.14-10	87.44	10.24	0.78	0.02	0.01	0.74	0.27	–	–	0.45	–	–
ST.15-10	90.92	5.05	2.45	0.05	0.54	0.69	0.29	0.01	–	0.01	–	–
ST.16-10	90.06	9.31	0.38	0.03	0.01	0.21	–	–	–	–	–	–
ST.17-10	90.54	6.94	1.04	0.42	0.01	0.89	0.15	0.01	–	–	–	–
ST.18-10	88.90	9.68	0.43	0.26	0.01	0.54	0.16	0.01	–	–	–	–
ST.19-10	90.27	8.18	0.38	0.18	–	–	–	0.15	0.20	–	–	0.20
ST.20-10	87.45	11.20	0.69	0.05	0.01	0.49	0.08	0.01	–	–	–	–
ST.21-10	91.69	6.90	0.72	0.04	0.01	0.52	0.10	–	–	–	–	–
ST.22-11	86.41	11.45	–	0.45	–	–	–	1.13	0.55	–	–	–

The varying bronze composition might have originated due to one of following processes of bronze production:

1. Co-smelting copper and tin ores in crucible to produce a bronze alloy [12,14],
2. Alloying by adding a variable amount of cassiterite (SnO_2) to the metallic copper and melting in crucible (cementation of metallic copper with cassiterite) [14–16].
3. Using a complex Sn-bearing copper ore [17].

In a co-smelting process, an admixture of sulphidic/oxidic copper ores and tine ore (cassiterite) are smelted in crucible to produce metallic tin bronze. The product is tin bronze with impurities. Also, alloy composition will vary with each smelting procedure. Second method implies adding the tin ore (SnO_2) to the melted metallic copper in a crucible. The product may be similar to what is obtained in the first method. Varying amount of cassiterite and the small size of bronze ingots produced in each smelting processes, results in bronze ingots with variable tin content and consequently, in bronze artefacts with different levels of tin [3,13,16,18–20]. Using a complex Cu–Sn ore may be another method of bronze production in the ancient time. Results of geochemical and metal analyses provide some evidences for smelting complex Cu–Sn ores from Deh Hosein to produce tin bronzes in the Luristan region during the Bronze Age of Iran at the third millennium BC [17,21]. But there is no evidence for the exploitation of the Deh Hosein ancient mine to extensive bronze metallurgy in the Luristan region during the first millennium BC. Nevertheless, each of the described processes may have been used for bronze production in the Luristan Iron Age bronze artefacts. In some cases, melting broken objects or imported bronze ingots is another method for bronze production but in view of the extensive bronze production in Luristan Iron Age and considering the high amount of bronze finds in this region, this is unlikely and it seems that bronze production would have existed as a local industry in western Iran.

As noted above, other metallic elements are identified as minor and trace elements. Only in some cases, the Pb amount is significant. Lead is insoluble in copper and appears as fine globules spread in the copper matrix. In the copper–lead system and during solidification of lead-containing copper, all of the alpha copper phase will solidify before the lead–copper eutectic is formed. Subsequently, it will cause the formation of Pb globules in the grain boundaries or within the grains of the copper solid solution [22–24]. Nevertheless, Pb may not be considered as an alloying element as it has been detected as a minor or trace element in many samples. Only in some cases it is present in about 2 wt.%., and in some published literature, a lead amount of more than 2% is considered as an intentional alloy component [25,26]. Lead may be considered as an intentional alloying addition even in low amounts, if it would be absent in the original copper ore [27] but usually, the prehistoric copper alloy artefacts in the Iranian Plateau have minor/trace amounts of lead that shows that it might derive as impurity from copper or tin metallic ores [5,28–30]. On the other hand, it may be due to the limitations of EDS as an analytical tool or concentration of lead globules in the analysed areas. In fact, the presence of lead was observed in the alloy, but the amount was not high enough to allow the total composition to change to a ternary Cu–Sn–Pb alloy, which was commonly used in metallurgy of same or later periods in different regions of the ancient world [31,32]. Also as noted above, in many ancient copper alloys from Iran, arsenic has been detected as an important alloying element, and indeed, many copper ores in Iran are As-bearing [1,3,12,33]. Nevertheless, arsenic is detected as a trace element in many samples which shows that the ore deposit used for metal smelting in this region has not been rich in arsenic. On the other hand, analytical investigations on some other bronze collections from Luristan Iron Age also shows the use of binary tin bronze alloy to produce metallic artefacts with low concentration of other elements such as Pb and As [2,34]. Thus, the copper ore deposits extracted for copper and bronze production in western Iran might not have contained considerable As concentration or copper arsenide minerals [12].

Chemical composition of three separate metal pieces from three vessels (ST.02-10/2, ST.09-10/2 and ST.10-10/2) shows that the spout and pins used for producing common spouted vessels in Luristan are also manufactured with binary Cu–Sn alloys similar to the alloy that is used for body production. The Sn amount is variable in these pieces and other elements are detected as minor/trace contents.

3.2. Microstructure

Metallographic samples of all bronze vessels were taken and examined under the optical microscope and SEM. SEM-BSE and optical microscopy (OM) micrographs of bronze samples before etching show very thin metal sheets with numerous scattered dark inclusions in metallic matrix that are elongated in latitude of cross section which

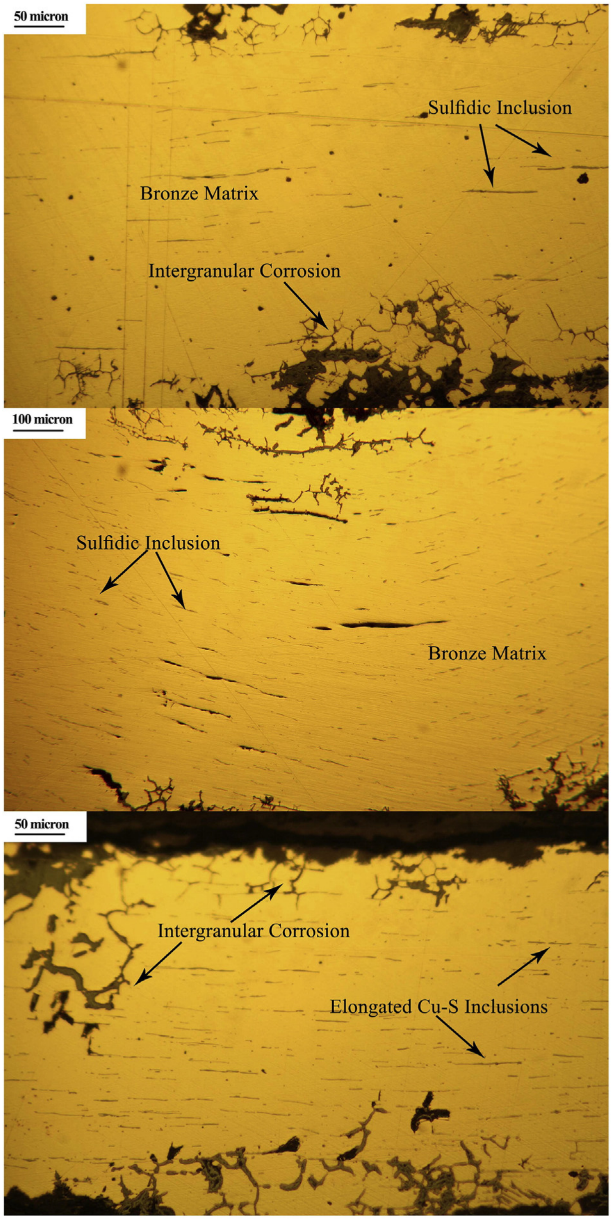

Fig. 2. Microstructure of some vessels before etching, including elongated copper sulphide inclusions and intergranular corrosion attacks distributed in bronze matrix.

appear as a grey-green colour in OM observations (Figs. 2, 3). The thickness of the metallic sheet in all samples is lower than 1 mm and in some areas reaches to about 300 μm. Only in the edges of the vessels a thickness more than 1 mm is measured. Some inclusions have remained unchanged in internal corrosion/oxidation layers under original surface of the metal objects. On the other hand, some very fine, globular bright inclusions are visible in the metallic matrix in high magnification BSE micrographs (Fig. 3). Also, corrosion layers have formed over the surface of the bronze samples. In some cases, these have penetrated the metal/corrosion interface as intergranular corrosion attacks along the grain boundaries. This phenomenon sometimes has caused formation of some pseudomorphic replacements of bronze microstructure with corrosion/oxidation products. The pseudomorphic replacements also partially reveal metallurgical and microstructural features of metallic grains such as strain lines or slip bands without intentional etching with chemical reagents (Fig. 3).

To reveal grains' microstructure and the manufacturing process, samples were etched in alcoholic $FeCl_3$ solution [22]. After etching, the microstructure of the bronze samples shows a typical grain structure consisting with worked and recrystallized grains of α solid solution of copper–tin with twinned and strain lines within the grains (Fig. 3). The twin lines usually are observed as straight. Strain lines are visible in some grains especially near the surface of the metal sheets. This microstructure is common in copper alloys and other FCC metals [22,35]. Based on the OM micrographs, grain size is not similar in all samples; also it is not homogeneous in all areas of each individual sample.

The metallographic studies on bronze samples state that all vessels are shaped during a cycle of cold working and annealing. This is apparent from equi-axed and recrystallized α-solid solution grains. In some cases, some slip lines are visible within the grains that may identify the final operation as cold working. Shaping by hammering on cold copper alloys may lead to a phenomenon named work-hardening. To remove this problem, the ancient metalworkers applied heat treatment (annealing) to return workability to the bronze piece. This heat treatment will improve the bronze mechanical properties because after mechanical work, a subsequent heat treatment would help to recover ductility, by promoting a recrystallization process [22,36,37]. In copper and its alloys, the heating temperature for annealing is 500–800 °C [22]. This operation causes the formation of a grain microstructure as observed in these vessels. Also, the amount of mechanical/thermal operation on the metal piece influences the grain size in the final product, meaning a smaller grain size may be due to more times of working and heating cycles. For example, the grain sizes in samples ST.08-10, ST.13-10 and ST.14-10 are apparently different (Fig. 4), and the grain sizes in sample ST.08-10 is more than 100 μm while it is 50 μm or less in two other samples. In fact, the samples with small grain sizes have been subjected to more working to reach the final shape and thickness [22].

All microstructures reveal the presence of numerous inclusions different in number, shape and size. To identify the chemical composition, some elongated and globular inclusions were analysed by SEM–EDS microanalysis. The results showed that the grey-green elongated inclusions are composed of copper and sulphur with a low content of iron and tin. Copper is detected as the major element within about 70–85% while sulphur is detected between 5 and 27% in different samples. Tin and iron concentrations are detected less than 10% in weight. The white inclusions in BSE micrographs are high lead metallic compounds with, in some cases, more than 70% of Pb (Fig. 5). Based on the Cu–Pb diagram [22], the chemical composition of Pb globules in Cu–Pb alloys is nearly a 100% of Pb and the presence of some copper, tin and iron in these inclusions might be due to influences from the surrounding phase compositions in the EDS microanalysis such as alpha copper solid solution matrix.

The presence of Cu–S inclusions in the bronze matrix may be due to using sulphidic copper ores for smelting and producing copper. Smelting copper sulphide ores has been common in ancient metallurgy to extract metallic copper [18,38,39]. In fact, some copper sulphides didn't transform to metallic copper during the smelting processes and are currently visible as small dark inclusions in the bronze microstructure; these may belong to unchanged original copper sulphide ores or these are by-product copper sulphide compounds that are formed during the smelting process but remained in the bronze microstructure, similar to products of matte production in the process of copper smelting [14,40]. These inclusions appear as segregated phases due to their low miscibility in molten copper [41]. A low iron amount in inclusions composition may be due to the presence of iron in copper ores or to use iron–copper sulphides such as chalcopyrite ($CuFeS_2$) [39]. It must be considered that, copper sulphide inclusions are more resistant than bronze alloy against corrosion/alteration events and remain unchanged in the internal corrosion layers (Fig. 3).

According to binary the Cu–Sn system equilibrium phase diagram, the maximum dissolution limit of Sn in Cu solid solution is 15.8 wt.% [22,35,36] and the α-copper phase would be the only phase in the microstructure of an alloy with up to 15% Sn when a homogenizing heat treatment, as annealing, is performed [37]. However, the common

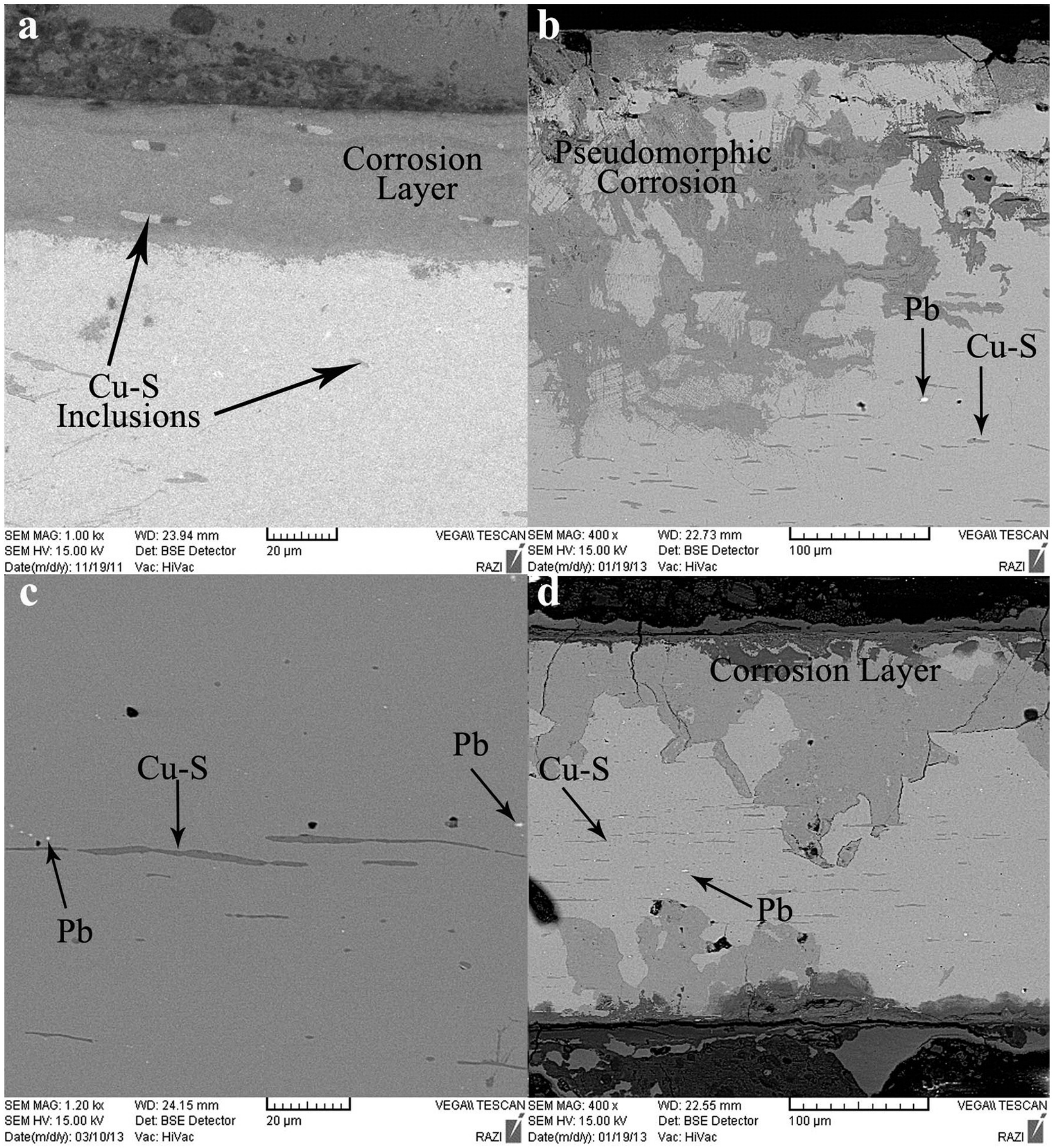

Fig. 3. SEM-BSE micrograph of bronze samples, copper sulphide inclusions, corrosion layers and pseudomorphic replacement are visible as well as fine lead globules.

dissolution limit of the tin amount noticed in literature for tin bronze objects is 14 wt.% and it is rare to find a tin bronze with higher amount of tin with a homogenous the α-solid solution phase [22,42]. Fig. 6 represents the specified area of Sn amount range determined in Sangtarashan bronzes in weight percent on the metastable (casting and annealing conditions) Cu–Sn diagram. According to the diagrams, in casting conditions two phases may be formed during solidification of bronzes with similar composition as the Sangtarashan bronzes: alpha solid solution and alpha + delta eutectoid while after annealing, only the α phase may be present in these bronzes and all eutectoid phase will transform to Cu–Sn solid solution during heat treatment [22,43]. The microstructure of samples shows a homogenous α solid solution without evidences of unchanged eutectoid phases besides the alpha phase. Only some circular inclusions or phases are visible in the sample ST.22-11 micrograph. EDS analysis showed that it has been composed with copper and tin, 62.34 and 33.90 wt.%, respectively, with a low amount of nickel, 3.76 wt.% (Fig. 7). It is an intermetallic Cu–Sn phase that may be formed due to some conditions during melt solidification and which is now visible as a segregated phase. Based on the Cu–Sn diagram (Fig. 6) and composition and microstructure of the intermetallic phases, it seems that it is composed by an alpha + delta eutectoid phase which is a common intermetallic phase in archaeological bronzes.

This eutectoid phase starts to appear as a result of segregation in the microstructure of low-tin bronzes (about 5% to 15% tin), depending on the cooling conditions of the alloy within the alpha dendrites in two-phased bronzes [22,36,42]. In the segregation of bronzes during solidification, usually alpha + delta ($\alpha + \delta$) eutectoid is the common intermetallic phase, but it has a permanent composition with 27% of tin [22,44–47], while the tin amount in the intermetallic phase of sample ST.22-11 is about 34%. This may be due to limitations of spot analysis by SEM–EDS. It could be interpreted by the metastable Cu–Sn diagram (Fig. 6), in which it is apparent that $\alpha + \delta$ eutectoid phase can be available beside alpha solid solution in the annealed condition in the Cu–Sn system [22,36].

The sample has 11.45% of tin. In bronzes with this Sn amount it is probable that intermetallic Cu–Sn compounds are formed due to casting operation. But in many cases, these phases could be removed by heating the bronze piece, e.g., during annealing [48]. In fact, in many cases thermomechanical operations lead to the removal of probable

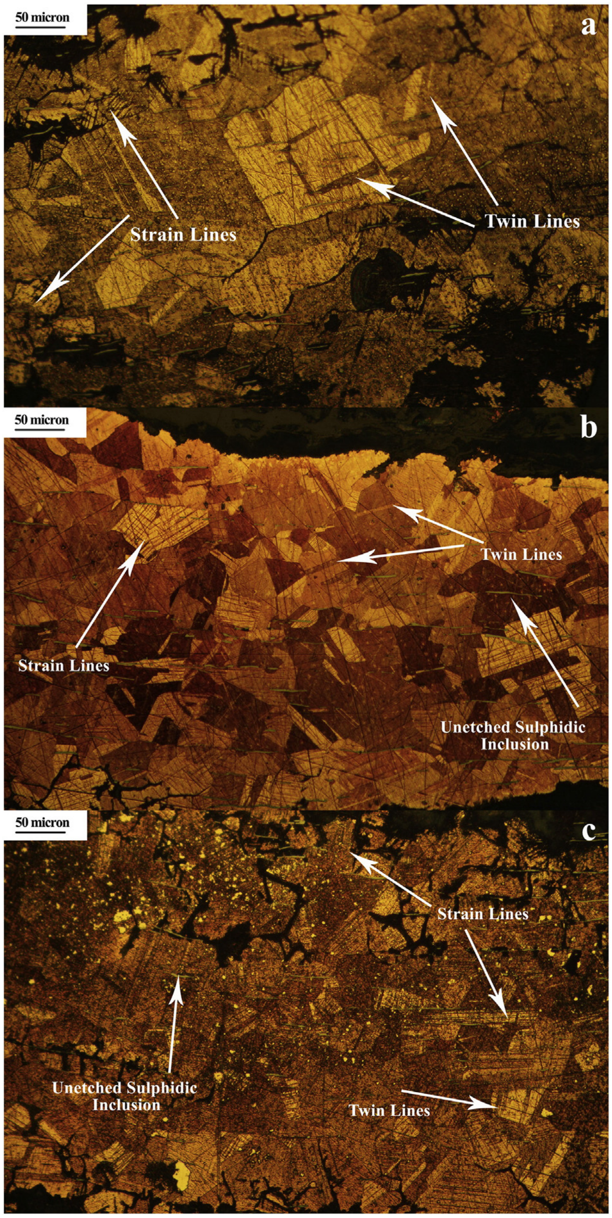

Fig. 4. Microstructure of three bronze vessels after etching in alcoholic $FeCl_3$, a) ST.08-10, b) ST.13-10, and c) ST.14-10, the microstructures are consisting of worked and recrystallized bronze grains with twinning and strain lines, the elongated sulphidic inclusions are visible unetched. The twin lines are usually straight; strain lines are visible more near the surface of the metal sheets and the grain size is variable in the samples.

segregations that occur in the metal structure during casting and solidification [22,36].

3.3. Bronze metalworking

Based on these results, smelting and metalworking processes in Sangtarashan Iron Age bronzes produce binary Cu–Sn alloys with some impurities such as Pb and As, as well as dispersed copper sulphide inclusions. In fact, the bronze alloy is obtained by smelting copper sulphides as copper ores. There are some possibilities for bronze production in this area and period but there is no absolute evidence for metallurgical activities in the Luristan region. As noted above, the bronze alloy may be produced by one of these processes: co-smelting, cementation or using complex Cu–Sn ores. With regard to literature, using complex Cu–Sn ores is attested in third millennium BC (Bronze Age) in Luristan [21,30] but there is no evidence for ore mining in the Luristan region from the Iron Age. Other proposed processes are also possible but no evidence is found by archaeological research in the Luristan region on archaeometallurgical activities of bronze production. Nevertheless, various amounts of tin in metal pieces may prove the application of an uncontrolled smelting system for tin bronze production during that time. Archaeometallurgical studies on some bronze artefacts in the Luristan style in some Iron Age sites in Western Luristan show a variety of Sn content as well as a low amount of other alloying elements in the composition. For example, Fleming et al. [34] analysed 22 bronze vessels from War Kabud site in Luristan beside some other bronze artefacts. The tin amount in these bronze vessels is between 2.6% and 18.2% and other elements are detected as minor/trace contents. Also, metallographic examination on a vessel from War Kabud presents a similar microstructure to the Sangtarashan vessels with twinned grains and some strain lines in the grains as well as elongated sulphidic inclusions dispersed in the bronze matrix [2,34]. On the other hand, analytic results of some Luristan bronzes in the Ashmolean Museum also provide the characteristics that are found in the alloy composition in the Sangtarashan bronze vessels [10]. Although, despite the large amount of Luristan bronzes in several museums, a hiatus about archaeometallurgical studies in this field is apparent in the literature.

The microstructure of bronzes showed that the metalworkers have applied mechanical operations and subsequent heat treatment to transform bronze ingots to final thin sheet metallic vessels. This is proved by the presence of worked and recrystallized grains, elongated inclusions and strain lines in some grains especially near surface of metallic sheets. Also, grain size is different in bronze samples and in several regions of one sample that implies a variety in degree of deformation used to shape the bronze vessels.

Thus, the microstructure and composition of the studied bronzes reveal that the following process can be suggested for these bronze artefacts:

1. Bronze production with co-smelting or cementation processes, perhaps in crucible to produce bronze prills with some impurities, the copper ores were sulphidic,
2. Melting bronze prills and producing bronze ingots,
3. Using ingots for casting sheets or pieces of bronze (optional),
4. Cold working on sheets or pieces to shape the vessels,
5. Annealing of work-hardened sheets to return workability,
6. A continuous thermo-mechanical process to reach the final shape of the vessels.

By this process, bronze vessels are manufactured with a microstructure and characteristics that have been explained above. Certainly, some small differences such as strain lines and grain sizes are present, but this manufacturing process can be suggested for all bronze vessels.

4. Conclusions

Microstructural study on some bronze vessels from the Sangtarashan Iron Age site in western Iran was carried out by microscopy and microanalysis methods. Results of 25 individual pieces from 22 vessels showed that all samples were manufactured with a variable composition of Cu–Sn or tin bronze alloy with some impurities such as lead and arsenic. In fact, chemical composition showed that the bronze production may have been performed by an uncontrolled production method, such as co-smelting or cementation, by using copper sulphide ores and tin oxide. Hereby bronze alloys with different tin amounts have been produced in each smelting process. Other elements such as Pb and As are considered as impurities that may derive from the original metallic ores. Specifically, the low arsenic content in the Luristan bronzes may entail the application of some specific copper ores apart from those used in the Chalcolithic/Bronze age of the Iranian Plateau. Also, the microstructure of bronze vessels shows the application of cold working (hammering) and subsequent heat treatment (annealing) as a cyclic procedure to transform a bronze

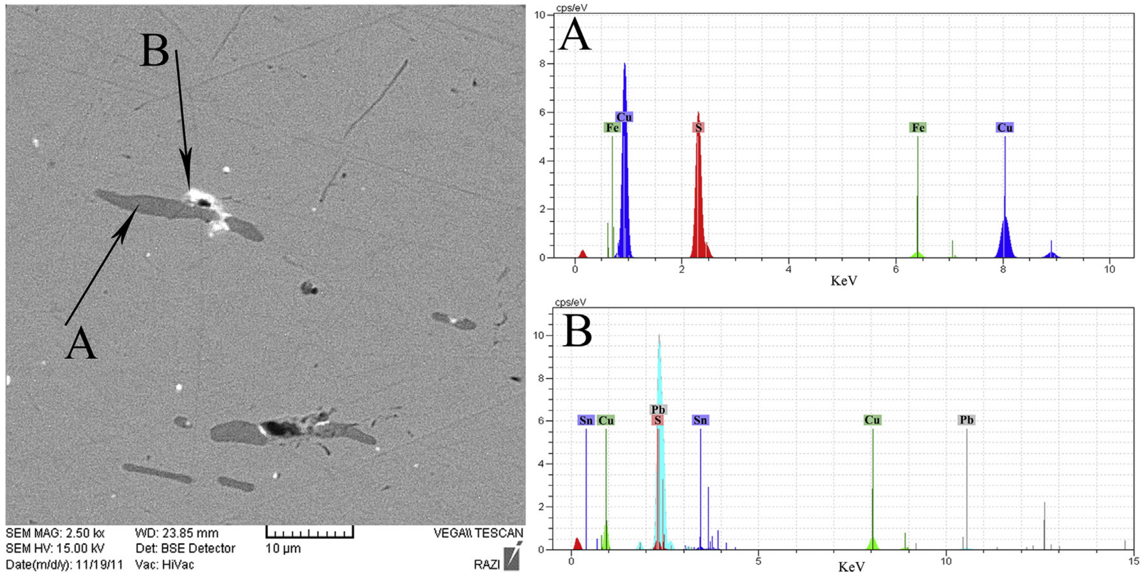

Fig. 5. SEM-BSE micrograph and SEM–EDS analysis of inclusions scattered in bronze matrix, elongated dark Cu–S inclusions (A) and, bright Pb globules (B) in sample ST.01-10.

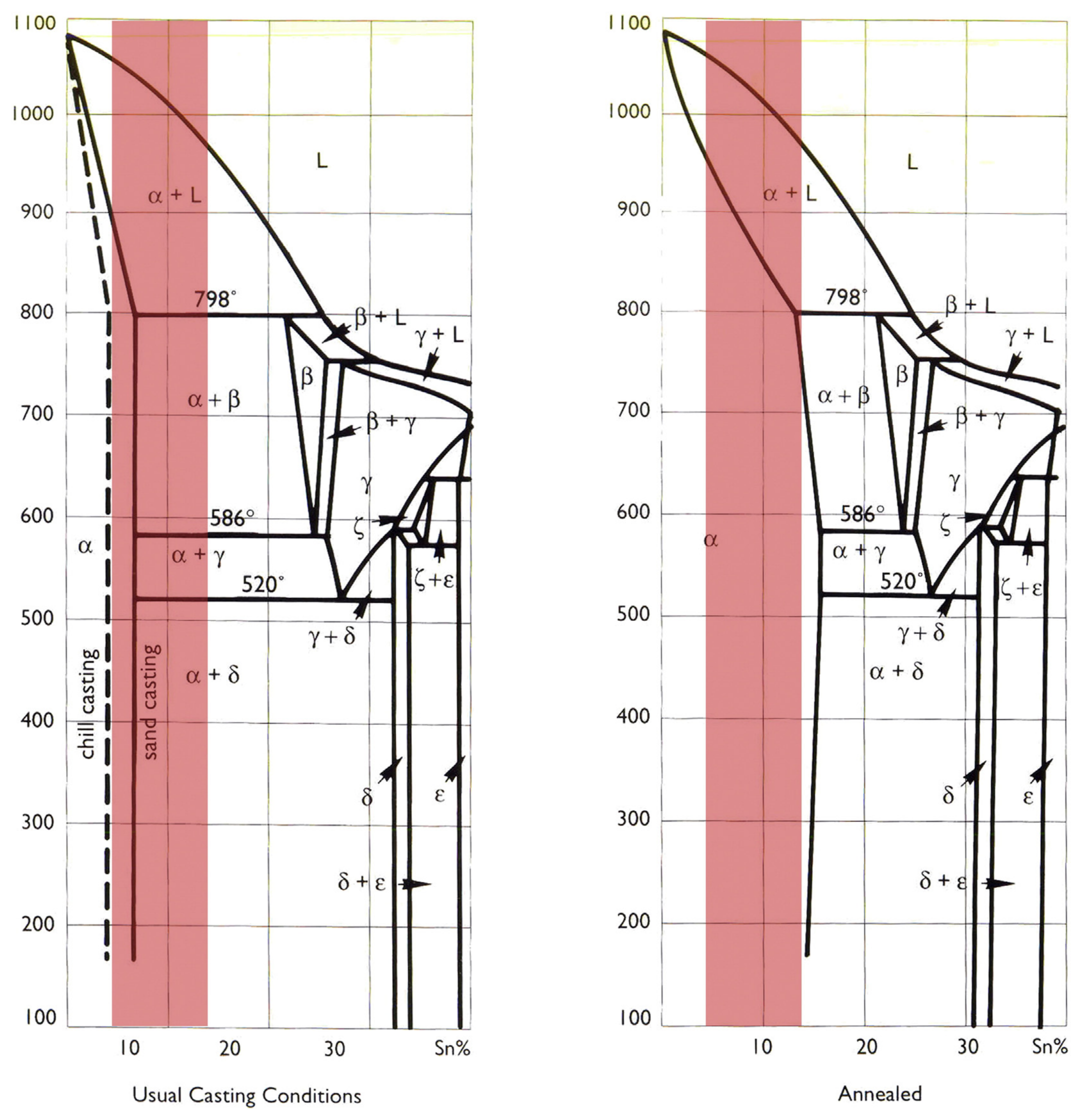

Fig. 6. Metastable Cu–Sn diagram, left) normal casting conditions, right) annealing conditions (after [22,43]). Range of determined tin in all bronze samples has specified on two diagrams and shows that two phases including alpha solid solution and alpha + delta eutectoid may form during solidification in casting condition, but in annealed condition, the eutectoid phase may transform to alpha solid solution in the specified range of Sn.

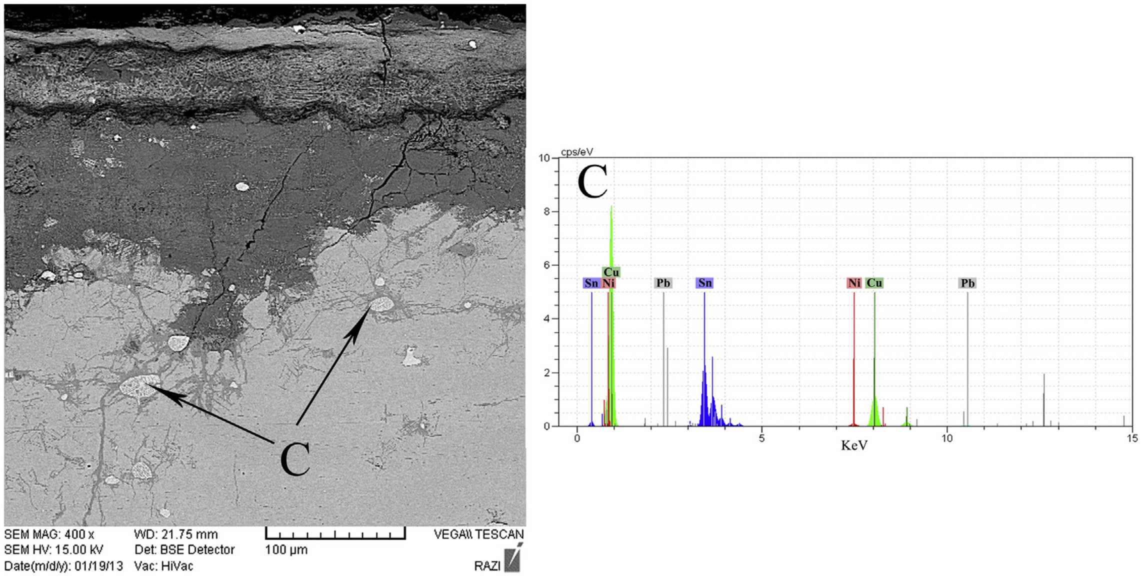

Fig. 7. SEM-BSE micrograph and SEM–EDS analysis of circular intermetallic phases in sample ST.22-11.

ingot into thin sheet vessels. The Significant issue is the similarity in composition and microstructure between the Sangtarashan bronze vessels and some other bronze artefacts (especially vessels) from other Iron Age sites in Luristan such as War Kabud. Finally, based on the results and their interpretations, the application of microscopic methods can help to establish manufacturing techniques and characteristics of archaeological metal artefacts.

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References

[1] C.P. Thornton, The emergence of complex metallurgy on the Iranian plateau: escaping the Levantine paradigm, J. World Prehist. 22 (2009) 301–327.
[2] S.J. Fleming, V.C. Pigott, C.P. Swann, S.K. Nash, Bronze in Luristan: preliminary analytical evidence from copper/bronze artifacts excavated by the Belgian mission in Iran, Iran. Antiq. XL (2005) 35–64.
[3] O. Oudbashi, S.M. Emami, P. Davami, Bronze in archaeology: a review of the archaeometallurgy of bronze in ancient Iran, in: L. Collini (Ed.), Copper Alloys—Early Applications and Current Performance-Enhancing Processes, InTech Open Access Publication, Rijeka, 2012, pp. 153–178.
[4] B. Overlaet, The chronology of the Iron Age in the Pusht-i Kuh, Luristan, Iran. Antiq. XL (2005) 1–33.
[5] P.R.S. Moorey, Archaeology and pre-Achaemenid metalworking in Iran: a fifteen year retrospective, Iran 20 (1982) 81–101.
[6] B. Overlaet, Luristan bronzes: I. The field research, in: E. Yarshater (Ed.), Encyclopaedia Iranica Online, 2006, (Originally Published: November 15 2006, http://www.iranica.com/articles/luristan-bronzes-i-the-field-research).
[7] B. Overlaet, Luristan metalwork in the Iron Age, in: T. Stöllner, R. Slotta, A. Vatandoust (Eds.), Persiens Antike Pracht, Bergbau Handwerk Archäologie, Exhibition Catalogue, Deutsches Bergbau-Museum, Bochum, 2004, pp. 328–338.
[8] O.W. Muscarella, Bronzes of Luristan, in: E. Yarshater (Ed.), Encyclopedia Iranica, IV, Routledge & Kegan Publications, London & New York, 1990, pp. 478–483.
[9] O.W. Muscarella, Bronze and Iron: Ancient Near Eastern Artifacts in the Metropolitan Museum of Art, Metropolitan Museum of Art, New York, 1988.
[10] P.R.S. Moorey, An interim report on some analyses of "Luristan bronzes", Archaeometry 7 (1964) 72–79.
[11] O. Oudbashi, S.M. Emami, M. Malekzadeh, A. Hassanpour, P. Davami, Archaeometallurgical studies on the bronze vessels from "Sangtarashan", Luristan, W-Iran, Iran. Antiq. XLVIII (2013) 147–174.
[12] V.C. Pigott, On the importance of Iran in the study of prehistoric copper-base metallurgy, in: T. Stöllner, R. Slotta, A. Vatandoust (Eds.), Persiens Antike Pracht, Bergbau Handwerk Archäologie, Exhibition Catalogue, Deutsches Bergbau-Museum, Bochum, 2004, pp. 28–43.
[13] V.C. Pigott, H.C. Rogers, S.K. Nash, Archaeometallurgical investigations at Tal-e Malyan: the evidence for tin-bronze in the Kaftari phase, in: N.F. Miller, K. Abdi (Eds.), Yeki Bud, Yeki Nabud: Essays on the Archaeology of Iran in Honor of William M. Sumner, University of Pennsylvania Museum of Archaeology and Anthropology, Philadelphia, 2003, pp. 161–175.
[14] P. Valério, A.M. Monge Soares, R.J.C. Silva, M.F. Araújo, P. Rebelo, N. Neto, et al., Bronze production in southwestern Iberian Peninsula: the Late Bronze Age metallurgical workshop from Entre Águas 5 (Portugal), J. Archaeol. Sci. 40 (2013) 439–451.
[15] M. Murillo-Barroso, T.O. Pryce, B. Bellina, M. Martinón-Torres, Khao Sam Kaeo — an archaeometallurgical crossroads for trans-asiatic technological traditions, J. Archaeol. Sci. 37 (2010) 1761–1772.
[16] E. Figueiredo, R.J.C. Silva, J.C. Senna-Martinez, M.F. Araújo, F.M. Braz Fernandes, J.L. Inês Vaz, Smelting and recycling evidences from the Late Bronze Age habitat site of Baiões (Viseu, Portugal), J. Archaeol. Sci. 37 (2010) 1623–1634.
[17] N. Nezafati, Au–Sn–W–Cu-Mineralization in the Astaneh-Sarband Area, West Central Iran, Including a Comparison of the Ores with Ancient Bronze Artifacts From Western Asia, (PhD Dissertation) Der Geowissenschaftlichen Fakultät, Der Eberhard-Karls-Universität Tübingen, Germany, 2006.
[18] H.H. Coghlan, Notes on the prehistoric metallurgy of copper and bronze in the old world, 2nd ed., Occasional Paper on Technology, 4, Oxford University Press, Oxford, 1975.
[19] D. Hosler, The Sounds and Colors of Power: The Sacred Metallurgical Technology of Ancient West Mexico, MIT Press, Cambridge, Massachuset, 1994.
[20] S. Rovira, I. Montero-Ruiz, M. Renzi, Experimental co-smelting to copper–tin alloys, in: T.L. Kienlin, B. Roberts (Eds.), Metals and Societies, Studies in Honour of Barbara S. Ottaway, Universitätsforschungen zur prähistorischen Archäologie, Habelt, Bonn, 2009, pp. 407–414.
[21] N. Nezafati, E. Pernicka, M. Momenzadeh, Ancient tin: old question and a new answer, Antiquity 80 (2006) 308 (http://antiquity.ac.uk/ProjGall/nezafati et al./index.html).
[22] D.A. Scott, Metallography and Microstructure of Ancient and Historic Metals, Getty Conservation Institute Publications, Los Angeles, 1991.
[23] C.P. Swann, S.J. Fleming, M. Jaksic, Recent applications of PIXE spectrometry in archaeology: I. Characterization of bronzes with special consideration of the influence of corrosion processes on data reliability, Nucl. Instrum. Methods Phys. Res. B 64 (1992) 499–504.
[24] R.J.C. Silva, E. Figueiredo, M.F. Araújo, F. Pereira, F.M. Braz Fernandes, Microstructure interpretation of copper and bronze archaeological artefacts from Portugal, Mater. Sci. Forum 587–588 (2008) 365–369.
[25] E. Figueiredo, M.F. Araújo, R.J.C. Silva, J.C. Senna-Martinez, Corrosion of bronze alloy with some lead content: implications in the archaeometallurgical study of Late Bronze Age metal artefacts from "Fraga dos Corvos" (North Portugal), METAL 07, ICOM-CC Proceedings, Amsterdam, 2008, pp. 61–66.

[26] E. Figueiredo, P. Valério, M.F. Araújo, J.C. Senna-Martinez, Micro-EDXRF surface analyses of a bronze spear head: lead content in metal and corrosion layer, Nucl. Instrum. Methods Phys. Res. A 580 (2007) 725–727.

[27] A. Charalambous, V. Kassianidou, G. Papasavvas, A compositional study of Cypriot bronzes dating to the Early Iron Age using portable X-ray fluorescence spectrometry (pXRF), J. Archaeol. Sci. 46 (2014) 205–216.

[28] C.P. Thornton, Of brass and bronze in prehistoric Southwest Asia, in: S. La Niece, D. Hook, P. Craddock (Eds.), Metals and Mines: Studies in Archaeometallurgy, Archetype Publications, London, 2007, pp. 123–135.

[29] M. Qorbāni, A. Kani, Copper II: Copper Resources in Iran, in: E. Yarshater (Ed.), Encyclopaedia Iranica Online, 2008, (Originally Published: April 7 2008, http://www.iranicaonline.org/articles/copper-ii-copper-resources-in-iran).

[30] N. Nezafati, M. Momenzadeh, E. Pernicka, New insights into the ancient mining and metallurgical researches in Iran, in: Ü. Yalçin, H. Özbal, A.G. Paşamehmetoğlu (Eds.), Ancient Mining in Turkey and eastern Mediterranean, Atilim University, Ankara, 2008, pp. 307–328.

[31] P.T. Craddock, The composition of the copper alloys used by the Greek, Etruscan and Roman Civilizations, 1. The Greeks before the Archaic Period, J. Archaeol. Sci. 3 (1976) 93–113.

[32] G.M. Ingo, T. De Caro, C. Riccucci, E. Angelini, S. Grassini, S. Balbi, et al., Large scale investigation of chemical composition, structure and corrosion mechanism of bronze archaeological artefacts from Mediterranean basin, Appl. Phys. A Mater. Sci. Process. 83 (2006) 513–520.

[33] C.P. Thornton, C.C. Lamberg-Karlovsky, M. Liezers, M.M. Young, On pins and needles: tracing the evolution of copper-base alloying at Tepe Yahya, Iran, via ICP-MS analysis of common-place items, J. Archaeol. Sci. 29 (2002) 1451–1460.

[34] S.J. Fleming, V.C. Pigott, C.P. Swann, S.K. Nash, E. Haerinck, B. Overlaet, The archaeometallurgy of War Kabud, Western Iran, Iran. Antiq. XLI (2006) 31–57.

[35] R.N. Caron, R.G. Barth, D.E. Tyler, Metallography and microstructures of copper and its alloys, ASM Handbook, Metallography and Microstructures, vol. 9, ASM International, 2004, pp. 775–788.

[36] D.A. Scott, Metallography and microstructure of metallic artifacts, in: B.W. Roberts, C.P. Thornton (Eds.), Archaeometallurgy in Global Perspective, Methods and Syntheses, Springer, New York, 2014, pp. 67–89.

[37] E. Figueiredo, J.C. Senna-Martinez, R.J.C. Silva, M.F. Araújo, Orientalizing artifacts from Fraga dos Corvos Rock Shelter in North Portugal, Mater. Manuf. Process. 24 (2009) 949–954.

[38] A. Hauptmann, The investigation of archaeometallurgical slag, in: B.W. Roberts, C.P. Thornton (Eds.), Archaeometallurgy in Global Perspective, Methods and Synthese, Springer, New York, 2014, pp. 91–105.

[39] H.G. Bachmann, The identification of slags from archaeological sites, Occasional Publications, 6, Institute of Archaeology, UCL, London, 1982.

[40] P. Craddock, Early Metal Mining and Production, Smithsonian Institution Press, Washington DC, 1995.

[41] P. Valério, R.J.C. Silva, M.F. Araújo, A.M.M. Soares, L. Barros, A multianalytical approach to study the Phoenician bronze technology in the Iberian Peninsula—a view from Quinta do Almaraz, Mater. Charact. 67 (2012) 74–82.

[42] N.D. Meeks, Tin-rich surfaces on bronze—some experimental and archaeological considerations, Archaeometry 28 (1986) 133–162.

[43] D. Hanson, W.T. Pell-Walpole, Chill Cast Tin Bronzes, Arnold, London, 1951.

[44] A. Paulin, S. Spaić, A. Zalar, N. Trampuž-Orel, Metallographic analysis of 3000-year-old Kanalski Vrh hoard pendant, Mater. Charact. 51 (2003) 205–218.

[45] M. Taube, Selective Dissolution in Copper Tin Alloys: Formation of the Surface Finish on Early Chinese Bronze Mirrors, (PhD dissertation) State University of New York, 1998.

[46] L.I. McCann, K. Trentelman, T. Possley, B. Golding, Corrosion of ancient Chinese bronze money trees studied by Raman microscopy, J. Raman Spectrosc. 30 (1999) 121–132.

[47] S. Srinivasan, I. Glover, Skilled mirror craft of intermetallic delta high-tin bronze ($Cu_{31}Sn_8$, 32.6% tin) from Aranmula, Kerala, Curr. Sci. 93 (2007) 35–40.

[48] J.S. Park, C.W. Park, K.J. Lee, Implication of peritectic composition in historical high-tin bronze metallurgy, Mater. Charact. 60 (2009) 1268–1275.