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Chemical and microstructural analysis of some Achaemenian silver alloy artefacts from Hamedan, western Iran

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Abstract

Precious metals have been often employed to manufacture various decorative artefacts at Pre-Islamic Iran. One of the most outstanding phenomena from this period of Iran was the extraordinary occurrence of the silver application to make various decorative objects. Indeed, application of silver and its alloys was extended for making different vessels and other decorative and royal objects in historic time, especially in Achaemenid (550-330 BC) and Sasanian (224-642 AD) Empires. In this paper, four silver artefacts dated to Achaemenid period, found in Hamedan region, Western Iran, are investigated to identify manufacturing/ shaping process as well as alloy composition. The examined objects consist of two bowls, one decorated plate and one decorated spoon with the head of a felidae. Scanning Electron Microscopy-Energy Dispersive X-ray Spectrometry (SEM-EDS) method has been applied on cross section samples to determine chemical composition of the alloys and the phases and optical microscopy (Metallography) and SEM techniques were used to study of microstructure and manufacturing/shaping procedure. The results showed that all samples were made of silver-copper alloys with different amount of copper in each artefact. Other elements have detected in minor/trace contents such as As, Pb, Cd, Al, S. The microstructure of samples showed interesting features that are related to manufacturing/shaping process to make silver artefacts and compositional aspects of the objects because of copper amount. In fact, two-phased microstructure could be observed in two Achaemenian silver bowls because of the high amount of copper in alloy composition. Two other artefacts include single phase microstructure depending on low content of copper in alloy composition.

Key words: Archaeometry; Achaemenid Period; Hamedan Museum; Silverworks; Ag-Cu alloys; Eutectic; Worked microstructure.

Introduction

The Achaemenid Empire (ca. 550-330 BC) is the first Persian kingdom in the Iranian Plateau extended from Anatolia and Egypt across western Asia to northern India and Central Asia. Achaemenid art is a ceremonial, religious and imperial art with high level skill that presents a world-wide scale, serving as a glorification of the dynasty. The peak of Achaemenid art came when the Persian power was at its height, with occurrence of gold and silver flowed into the royal treasury from the all regions of the empire and the kings of the dynasty constructed large and fine palaces and capital cities such as those that are in Susa and Persepolis. In general, Achaemenid art is a complex of many elements belonging to various origins and traditions since materials, masters and artisans were brought from all provinces under its rulership such as Babylonians, Assyrians, Egyptians and etc (Schmidt, 1983; Calmeyer, 1986).

The Achaemenian metalworking is one of the significant industries and arts with very famous examples. During Achaemenid period, ancient metalworking traditions continued, with considerable stylistic elaboration. The main characteristic of Achaemenian metalworking is to use precious metals to manufacture individual artistic royal objects besides applying other metals such as iron and copper alloys for routine, military and daily-use artefacts (Ghirshman, 1964; Muscarella, 1988; Pigott, 1990). Application of gold and silver to make various objects caused the formation of an individual metalworking style that have been under influence of art of all regions and nations that were under rulership of the Achaemenids. These metal artefacts are produced in a high level manufacturing procedure and technology with various shapes and dimensions. Bowls such as different Phiales and Rhytons, the Treasury of Oxus, silver spoon from Pasargadae (the first capital of Achaemenid dynasty) and

other decorated objects (Figure 1) are some considerable examples concerning the use of precious metals in the Achaemenian period (Ghirshman, 1964; Stronach and Gopnik, 2009; Mongiatti et al., 2010). Especially, gold has been employed for a variety of uses, including coinage, weaponry, ornament, furniture, and vessels (Ross, 2001). In general, little Persian gold and silver objects have been discovered in archaeological excavations from Persia itself; the exceptions are discoveries at Susa (de Miroschedji, 1990) and Pasargadae (Stronach, 1978).

Apart from development and importance of gold/silver metallurgy in the Achaemenid period, some limited technical studies have performed on precious metals to identify metallurgical aspects and manufacturing techniques in gold and silver metalworking at this time such as some analyses published by Gunter and Jett (1992) on a silver plate (Phiale) from Freer Gallery of Art, a gold four-horse model chariot from the Oxus Treasure, now in the British Museum by Mongiatti et al (2010), and some analyses and explains about some gold objects from the Oxus Treasure published by Armbruster (2010) and Cowell (2003), scientific examinations on two silver bowls from British Museum published by Simpson et al. (2010) and some Achaemenian silver and gold pieces from Babylonia (Hughes, 1986). In fact, studies considered with Achaemenian precious metals in general focus on style and art aspects whereas technological and metallurgical subjects are rarely considered.

In this paper, four Achaemenian silver objects from the properties of Ebn-e Sina (Avecina) Museum of Hamedan, western Iran were selected for examination by analytical and microscopic investigations. The aim of this paper is an investigation of manufacturing processes to produce metallic objects of silver and its alloys during the Achaemenid era to develop archaeometallurgical investigations in



Figure 1. Some gold and silver objects belonging to the Achaemenid period, a) gilded silver jar with handles decorated with ibexes, b) silver plate decorated with radiating lobs and petals, c) silver jar with handles decorated with ibexes, d) silver spoon with swan's head handle, Pasargadae, e) gold vase with beaded surface, f) silver plate with large lobes and g) gold rython with lion head and gold sword both from Hamedan; a and g (Porada, 1963), b, c, e and f (Stierlin, 2006), d (Stronach, 1986).

the Iranian Plateau. In fact, the Achaemenid era is an important period in history of Iran while metallurgical aspects at that time need to do more experimental studies to reveal different features of this technology in Iran. Also, using precious metals has developed in that time and some examples of gold and silver artefacts were found in archaeological activities at Achaemenian sites. In 2012, a conservation project designed and operated to an individual metal collection

in Ebn-e Sina (Avecina) Museum, Hamedan, western Iran, consisting of various metallic artefacts under auspice and support of ICHTTO of Hamedan province as well as Museums Office of ICHTTO. The project includes conservation operation on about 400 different metal artefacts which made by different copper alloys as well as silver and iron. The metal collection is dated to from Prehistoric to Islamic periods. This study is a part of the extensive technical investigation of the large-scale conservation project of the metal collection, Ebn-e Sina Museum of Hamedan, western Iran (Oudbashi et al., 2014).

Materials and Methods

For the present study, four silver objects belonging to Ebn-e Sina Museum of Hamdean were selected (Figure 2). These are consisting of two bowls (B-1 and B-2) with simple decorations on their surface, one smooth plate (P-1) with typical Achaemenian decorations, and one spoon with the head of a felidae on the end of its handle. Based on archaeological investigations and artistic styles, these are dated to the Achaemenid period. In fact, these examples are typical and common objects at that period and some similar examples are found that are belonging to the Achaemenid period (Porada, 1963; Stierlin, 2006; Stronach, 1986; Shapur Shahbazi, 2004; Ross, 2001), for example see other Achaemenian objects presented in Figure 1.

To study of the silver metalworking in the Achaemenid period, an experimental process was established based on characterization of some Achaemenian silver objects by using microscopy and microanalysis methods. The aim of application of this process was to identify chemical composition of alloys, determining phases and inclusions as well as to characterize the microstructure of metal samples before and after etching (Figure 3).

A small sample from each object was cut and cold-mounted using a two-part epoxy resin (resin and hardener) and cross-sectioned by grinding with abrasive papers (400-2000 grid) and then polishing with diamond pastes (from 6 to 0.5 microns) (Scott, 1991). The sampling was done from broken parts of the objects.

SEM and EDS investigations were carried out by means of a TESCAN model VEGA II XMU in low vacuum, with a RONTEC backscattered electron detector (BSE) and an energy dispersive spectrometer (EDS) on mounted and polished samples in order to observe and analyse metal matrix, inclusions and details of microstructure in high magnifications. In addition, microstructure of samples before and after etching by acidified potassium dichromate solution (Scott, 1991) were observed by using a polarized light microscope BK-POL/BKPOLR model manufactured by Alltion Company, China.

Results

The OM and SEM-BSE micrographs of silver samples showed that the two bowls (B-1 and B-2) are made of two separate thin metal sheets. Some corrosion products are formed on the surface and between two metal sheets in red or green colours (Figures 4 and 5). A multilayered microstructure consisting of very fine and slime bright and dark layers is apparently visible in optical microscopy (OM) photos of each thin metal sheet. The multilayered structure can be observed apparently by optical microscopy as metallic dark and bright thin layers in both BFOM and DFOM illuminations. These layers are elongated through the section longitudinally and are also visible as dark and bright phases that are indicated in red colour in SEM-BSE micrographs (Figure 6). Some separations were occurred in two thin metal sheets due to corrosion or embrittlement in which red corrosion products are formed. The corrosion layers are visible as thick red crusts especially between two metal sheets and some thin green



Figure 2. Four silver objects from Ebn-e Sina Museum, Hamedan, B-1 and B-2: large silver bowls, S-1: spoon with the head of felidae decoration and P-1: silver plate with lob and petal decorations.

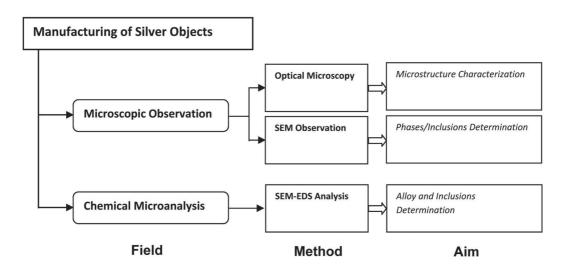


Figure 3. Analysis protocol and process of study on silver objects performed in this investigation.

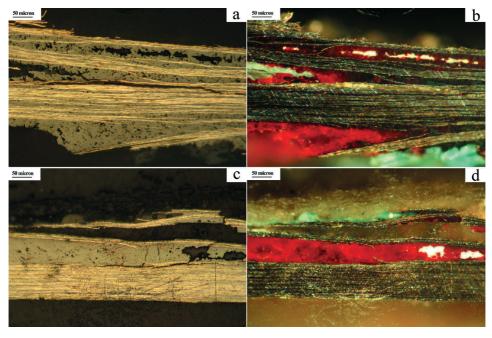


Figure 4. Microstructure of samples B-1 and B-2, a) BFOM and b) DFOM micrographs of sample B-1 and c) BFOM and d) DFOM micrographs of sample B-2, consisting of apparent two metal sheets, internal corrosion layer, lamellas and thin layers showing two phased structure and some breakings in metallic lamellas.

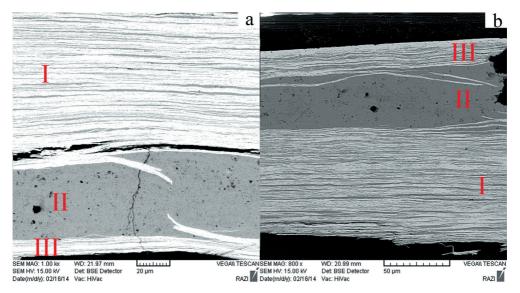


Figure 5. SEM-BSE micrograph of the bowls, a) B-1 and b) B-2, showing two phased microstructure with thin layers and the presence of two sheet metals with corrosion between them.

Table 1. Chemical Composition (wt%) of alloy, phases and inclusions in four Achaemenian silver artefacts.

Sample	Analysis	Ag	Cu	As	Pb	O	Cl	S	Au	Ni	Cd	Al
B-1	I	61.16	30.46	0.10	0.01	8.26	_	-	-	_	_	-
	II	0.44	85.55	_	-	13.81	0.20	_	_	_	_	_
	III	65.21	29.07	0.07	_	5.65	_	_	_	_	_	_
	IV	6.30	82.19	0.12	0.60	9.59	_	0.03	0.54	_	0.64	_
	V	79.93	17.55	0.13	_	2.09	_	0.19	0.10	_	0.01	_
B-2	I	67.14	24.98	0.05	0.42	6.99	_	0.11	0.31	_	_	_
	II	0.40	87.42	0.04	0.09	11.78	_	_	_	0.27	_	_
	III	59.82	30.73	1.62	0.27	6.89	_	0.09	0.56	_	_	_
P-1	I	97.61	1.85	0.06	0.12	_	-	0.04	_	0.32	_	_
S-1	I	91.33	1.95	2.11	0.03	_	_	0.04	0.32	_	3.60	0.61
	II	21.90	1.41	0.50	69.40	6.75	_	0.01	0.01	_	0.02	

layers over the surface (Figure 5).

Semi-quantitative SEM-EDS analysis was performed to identify the chemical composition of two separate metal sheets existing in two silver bowls and the results are presented in Table 1 (analyses I and III of samples B-1 and B-2). Based on Table 1 it is apparent that two thin metal sheets are made with a silver-copper alloy, silver is variable from 61.16 to 65.21 (wt%) in sample B-1 and 59.82 to 67.14 (wt %) in sample B-2. Also copper is present in 30.46 and 29.07 wt% in two sheets of sample B-1 and 24.98 and 30.73 wt% in sample B-2 respectively (analyses I and III in both samples). In sample B-1, arsenic and lead are detected as trace elements while oxygen is determined as a main component. In sample B-2, As, Pb, S and Au are detected as minor and trace amounts. The important matter is that in layer III arsenic is measured in 1.62 wt%. Also, the concentration of oxygen is significant in composition of two metal sheets of sample B-2.

Analysis of corrosion layers formed between two metal sheets of samples B-1 and B-2 (analysis II in Figure 5) was also performed by

SEM-EDS method (Table 1). Results showed that the layer II is chemically similar in two samples and Cu and O are the main constituents in the composition of the layers. Of course, copper amount is very higher than oxygen and can be calculated about 7 times as much oxygen amount. On the other hand, the amount of silver is very low and measured less than 0.5% wt% and states that silver don't play a specific role in the composition of the corrosion layer formed between metal sheets. In fact, the corrosion layer occurred between the metal sheets in two bowls (B-1 and B-2) is a copper corrosion compound that regarding to its colour (Figure 4) may be copper oxide, cuprite (Cu₂O), in this case. Other elements such as Cl, As, Pb and Ni also are determined as minor and trace amounts in corrosion layers composition.

To identify the chemical composition of two elongated lamellar phases observed in the SEM-BSE micrographs, they were analysed by SEM-EDS microanalysis method in sample B-1. Results showed that the dark layers are Cu-rich phase (analysis IV, Table 1, Figure 6) while the bright phases are Ag-rich compounds

(analysis V, Table 1, Figure 6). The Cu-rich phase (IV) contains 82.19 % of copper and 6.30% of silver respectively, and the Ag-rich component (V) is composed with 79.93% of silver and 17.55% of copper. Oxygen is detected as a major component in two individual phases (analyses IV and V of sample B-1), although the oxygen amount is measured in the copper rich phase (IV) more than the silver rich one (V). Other elements are detected as minor and trace amounts such as As, Pb, S, Cd and Au (Table 1).

Samples P-1 and S-1 also were analysed by using SEM-EDS (Table 1, Figure 7). The results showed that these samples are made of a silver-copper alloy with low amount of copper (analysis I of samples P-1 and S-1). Sample P-1 contains 97.61% of silver and 1.85% of copper. Other elements are detected as minor or trace amounts. On the other hand, the main elements in sample S-1 are Ag, Cd, As and Cu respectively. Other elements also are detected as impurities. Presence of quite significant

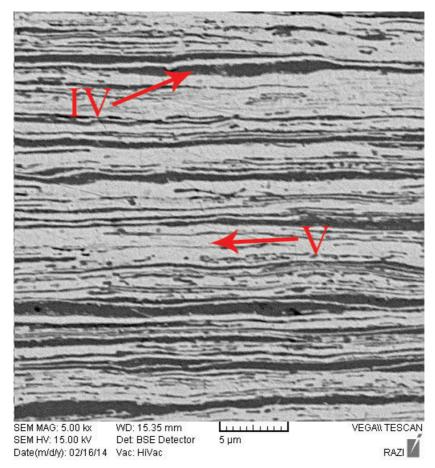


Figure 6. SEM-BSE micrograph of sample B-1 showing two apparent elongated copper rich (analysis IV) and silver rich (analysis V) phases.

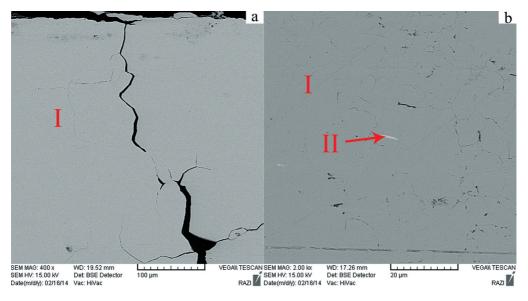


Figure 7. SEM-BSE micrograph of samples a) P-1 and b) S-1, intergranular cracking is visible, especially in P-1, the elongated bright phase in sample S-1 (analysis II) is lead particle.

amounts of cadmium and arsenic in this sample is very remarkable because they have detected in amounts more than copper. The bright, elongated inclusions are also visible in the metallic matrix of sample S-1 that they are Pb-rich phases based on SEM-EDS results (analysis II).

To characterize the grain structure in two samples P-1 and S-1, cross sections were etched in acidified potassium dichromate solution (Scott, 1991). The microstructures after etching are presented in Figure 8. The microstructure of two samples is consisting of worked grains in which some straight twinning lines are visible in sample P-1. On the other hand, the grain size is different in two samples; grains are large in sample P-1 while a very smaller grain size could be observed in the etched microstructure of sample S-1.

It is not possible to observe other microstructural features in sample S-1, such as twin lines, due to fine and small grain size of the sample. Also, some cracks and elongated holes are visible in the grain boundaries of these samples. Based on SEM-EDS analyses, these samples are low-copper silver alloys with less than 2% of copper and there are no evidences about occurrence of two phased microstructure, in fact these silver alloys are including one silver-copper metallic phase.

Discussion

Chemical analysis of four Achaemenian silver objects showed that all objects are manufactured by silver-copper alloys with different amount of copper and some other metallic elements as impurities. Only in two samples, arsenic is detected as considerable amount.

Based on chemical composition, alloy in four Achaemenian silver objects could be categorized in two specific groups, low-copper silver alloy and high-copper (or debased) silver alloy. Figure 9 shows the diagram of the Ag/Cu proportion in two silver sheets of samples

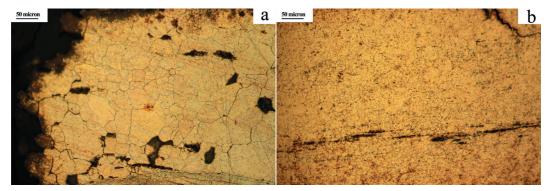


Figure 8. OM micrograph of etched microstructure of samples, a) P-1 and b) S-1. The grain size is apparently different in two samples. Some straight twin lines are partially evident in grains of sample P-1.

B-1 and B-2 and in samples P-1 and S-1. The diagram states that two metal sheets in samples B-1 and B-2 have similar composition and can be placed in a category while other silver artefacts are produced by a silver-copper alloy with less that 2% of copper. The silver was debased to some extent with copper, partially to produce the alloy harder and also to reduce the amount of silver because silver was expensive and rare in the ancient times (Scott, 1991). In fact, many debased silver artefacts are made of silver-copper alloys and both constituents are clearly visible in the polished and etched section; they show up a two phased system as a copperrich phase and a silver-rich phase (Taylor, 2013; Scott, 1991; Northover et al., 2014).

Figure 10 shows the equilibrium diagram of Ag-Cu system and approximate location of alloy composition in samples withdrawing other detected elements. The diagram is prepared and normalized based on Ag + Cu = 100% in the alloy composition of all samples. Other major, minor and trace elements detected in their composition are not considered in total composition. In fact, all samples are considered as pure Ag-Cu alloys without any impurities in this diagram. Further, six lines for alloy compositions are placed in the diagram, four of sheet metals from B-1 and B-2 bowls, and two from P-1 and S-1objects.

The diagram shows that alloy in samples B-1 and B-2 is near the eutectic composition while other artefacts are placed in Ag-rich β region of the solid solution. The silver-copper alloys are one of the famous examples of the eutectic structure. The microstructure of such silver alloys with copper amount about 20% or more (similar to two Achaemenian bowls) is consisting of a mixture of copper rich (α) phase and silver rich (β) phase. Although, the microstructure of two silver bowls (B-1 and B-2) is observed in unetched conditions by OM and SEM techniques, however, the twophased microstructure of the two silver bowls including elongated metallic copper and silver rich phases is visible apparently in microscopic illumination.

On the other hand, two low-copper silver artefacts may be consist of a microstructure including $\beta+(\alpha+\beta)$, according to the diagram, but there is no evidence of formation of second metallic phase in these samples that may be occurred due to cooling conditions that has led to the formation of low-copper β solid solution of silver (Scott, 1991).

One of the interesting matters in samples B-1 and B-2 is morphology of two elongated phases. It can occur when a two-phased alloy (in this case, Ag-Cu alloy) is worked that either one or

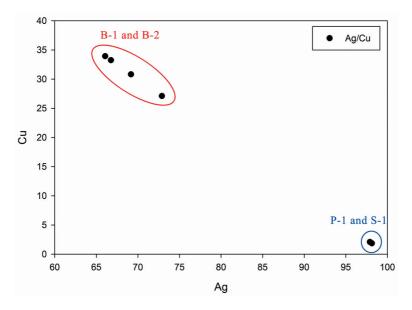


Figure 9. Ag-Cu proportion in both sheets of samples B-1 and B-2 as well as P-1 and S-1. The diagram states that samples B-1 and B-2 are made of debased silver-copper alloys while P-1 and S-1 are low copper silver alloys.

both phases can become elongated or strung out, along the direction of the working of the alloy (Scott, 1991). This microstructure is due to the presence of the phases in a eutectic alloy and is named as fibrous (Scott, 1991) or banded microstructure (Gibbons et al., 1974). Figure 11 shows two alloys with eutectic structure. At left, the eutectic phase and dendrites are formed in a typical eutectic cast alloy, such as high-copper silver alloy, in which alpha phase dendrites are formed and surrounded with eutectic phase $(\alpha+\beta)$. Formation of dendrites in FCC metals in the presence of impurities or alloying elements is usual. In fact, in the case of silver-copper alloys, this kind of microstructure may form in chemical composition near eutectic point (e.g. about 72% of silver) (Gordon et al., 2007; Scott, 2010). Amount of eutectic phase in such microstructures follows by chemical composition, at the eutectic composition

(eutectic point in phase diagram), the liquid melt passes directly to solid and ideally will consist of a fine, intermixed matrix of α and β phase. In many cases, working or mechanical operations would be next stages to shape metal artefacts. Working may change the microstructure of eutectic containing alloys and may lead to formation of fibrous morphology consisting of elongated dendritic and eutectic phases like what is presented in Figure 11 that shows the eutectic alloy that has been worked heavily. In fact, the microstructure of samples B-1 and B-2 is consisting of an alpha copper rich phase that includes less part of the alloy and a more eutectic silver rich phase. Of course, the formation of the significant amount of alpha dendritic phase in these samples is due to amount of copper in alloy composition more than eutectic composition.

In the chemical composition of lamellas, a considerable amount of oxygen is detected. It

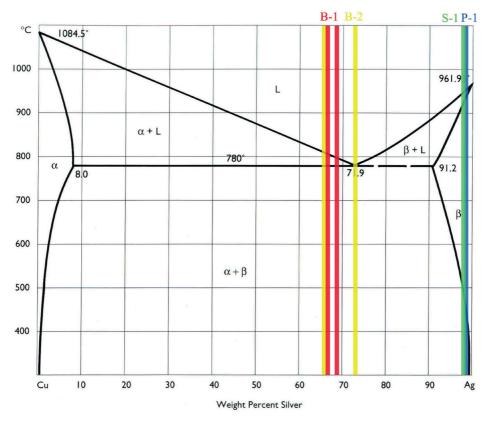


Figure 10. Equilibrium phase diagram of Silver-Copper with characterizing Ag-Cu alloy composition in six alloy composition from four Achaemenian samples (after Scott, 1991). The diagram is prepared regarding to the proportion Ag+Cu=100% and the alloy composition is considered as a pure Ag-Cu alloy. Other major (such as oxygen) and trace elements detected in the alloy composition of all samples are overlooked in preparing this diagram.

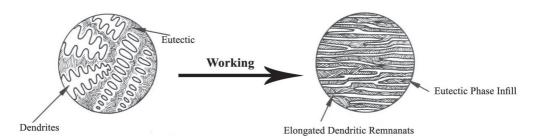


Figure 11. Typical morphology of two-phased microstructures of eutectic alloy: left) cast alloy with dendrites, right) worked alloy with elongated or banded microstructure (After Scott, 1991).

can be referred to formation of metallic oxides in the layers. In many cases, metallic oxides form on the surface of metallic artefacts, but in this specific case, formation of copper oxide in internal structure of metallic object is usual. This phenomenon is referred in associated with annealing depending on the metal concerned. For example, when debased silver alloys (e.g. samples B-1 and B-2) are annealed by heating in air (a common heat treatment applied to ancient metals to return workability), they are likely to suffer internal oxidation. During annealing, a black skin of cupric oxide or tenorite (CuO) forms, overlying a subscale of cuprous oxide or cuprite (Cu₂O), while oxygen can diffuse into the underneath alloy, attacking the readily oxidized copper rich phase and producing internal cuprite embedded in a silver-rich matrix (Scott, 2010; 1991). Thus, the presence of high amount of oxygen in alloy composition of two silver samples (B-1 and B-2) as well as the copper rich phase in sample B-1 can be explained by performing annealing operation during the manufacturing process of vessels. It has been applied to produce very thin sheet vessels and remove work hardening occurred during mechanical operations.

Further, in Ag-Cu alloys, such as debased silvers, long term corrosion may lead to a localized galvanic attack of the less noble copper-enriched regions. It will lead to leach copper from alloy microstructure and its redeposition on the surface as copper corrosion products (Wanhill, 2003). In the long term corrosion of silver-copper alloys, copper is leached from object due to selective corrosion. Copper, as a chemically active metal can form a large number of compounds re-deposited on the surface of archaeological silver alloy artefacts as corrosion products (Viljus and Viljus, 2012; Domenéch et al., 2012; Ingo et al., 2006). The presence of cuprite (Cu2O) on the surface and between the metallic sheets is due to selective corrosion of the main alloying element, which

is re-deposited after dissolution onto the surface of the Ag-Cu sheets, thus forms a copper enriched layer that is observed in SEM and OM micrographs (Ingo et al., 2006). In fact, Presence of the copper compounds in the Ag-Cu alloy objects (red corrosion layers in B-1 and B-2) may be due to corrosion events occurred in the copper constituent during burial time.

other samples have different characteristics that caused to formation of different microstructures. Based on the phase diagram of Ag-Cu (Figure 10), chemical composition of samples P-1 and S-1 are placed in the β silver rich and $\alpha+\beta$ regions. Of course, because solidification in alloys in common conditions do not conform from equilibrium conditions such as what that is presented in phase diagrams, practically, Ag rich β solid solution is the main phase that forms during cooling in a low copper silver alloy, although the occurrence of segregation and formation of low amount of high silver eutectic phase in the grain boundaries is probable based on the cooling conditions. These silver alloys are considered as low copper silver alloys. The addition of copper to silver has been a common way to make silver harder, because pure silver is so soft (Scott, 2010). Of course, the achieved hardness is related to the copper amount added to silver. On the other hand, etched microstructure of these samples varies with two silver bowls that have explained. The microstructure is consisting of the worked grains with different size in two samples. In sample P-1, the grains are large and some straight twin lines are visible in etched grains while the grain size in S-1 is very fine and no twin or other microstructural features are visible in microscopic magnification (about 200X). Nevertheless, these types of microstructure forms in FCC (low copper silver) metals due to application of working and annealing to shaping and finalize the artefacts (Scott, 1991; 2010; Pistofidis et al., 2006; Gordon et al., 2007; Northover et al., 2013). In

fact, a cycle of cold working (hammering) and heating (annealing) applied to produce these silver objects. Application of annealing after working to remove work hardening occurred in alloy leads crystal reform by twinning operation that results to make twinned grains. Whatever more cycle of working/annealing operates on the artefact, the finer and smaller grain size occurs. Indeed, the difference between grain size in two samples may be explained with various amounts of working or working/annealing applied on the artefact for shaping. Also, some intergranular and transgranular crackings are visible in the microstructure of sample P-1 and S-1 (Figures 7 and 8). These crackings are referred in the literature depending on whether there is retained cold work in the silver and are named as stress corrosion cracking in archaeological silver. In fact, a mixture of stress produced by cold working that has not removed by annealing, pressure or corrosion attacks during burial times in soil and probable segregation of copper in grain boundaries may have led to formation of cracks in microstructure of these silver artefacts (Wanhill, 2003; 2013; Vaníčková et al., 2008).

Conclusions

Application of precious metals to produce decorative artefacts in the Achaemenid period is reviewed and four Achaemenian silver artefacts are studied to determine manufacturing process based on chemical and microscopic investigations. Two different alloys are detected for produce ancient silver objects: high copper debased silver alloy with about 25-30% copper to make thin sheet bowls and low copper silver alloy with about 2% copper in the plate and the spoon. Application of silver alloys with different amount of copper has led to formation of different microstructure in artefacts that caused to the occurrence of eutectic microstructure in debased silver alloys. Also, microstructure of samples shows the application of mechanical procedure with subsequent heat treatment (annealing) to make transformations in the initial cast silver alloy. In fact, all samples are affected by a cycle of cold working/annealing to shape final artefact. The results state variety of manufacturing processes used to production of silver objects during the Achaemenid period.

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References

Armbruster B.R. (2010) - Technological Aspects of Selected Gold Objects in the Oxus Treasure. In: The World of Achaemenid Persia, History, Art and Society in Iran and the Ancient Near East, (Eds.): J. Curtis and S.J. Simpson, Proceedings of a Conference at the British Museum, 29th Sept.- 1st Oct. 2005, I.B.Tauris, London, 397-408.

Calmeyer P. (1986) - Art in Iran III: Achaemenid Art and Architecture. In: Encyclopædia Iranica, II, 6, 569-580.

Cowell M.R. (2003) - Analysis of gold plaques from the Oxus Treasure', in Culture through objects: ancient Near Eastern studies in honour of P. R. S. Moorey, (eds.) T. Potts, M. Roaf and D. Stein, Griffith Institute, Oxford, 241-244.

de Miroschedji P. (1990) - Note d'orfèvrerie Neo-Elamite. In: Contribution à l'Histoire de l'Iran, (ed.): F. Vallat, Paris, 181-194.

Domenéch A., Domenéch-Carbó M.T., Pasies T., del Carmen Bouzas M. (2012) - Modeling Corrosion of Archaeological Silver-Copper Coins Using the Voltammetry of Immobilized Particles. *Electroanalysis*, 24, 1945-1955.

Ghirshman R. (1964) - The Art of Ancient Iran from its Origins to the Time of Alexnader the Great, Translated by Sturat Gilbert and James Emmons.

- Golden Press, New York.
- Gibbons D.F., Ruhl K.C. and Staikoff L.S. (1974) -Analysis of Sasanian Silver Objects: A Comparison of Techniques. In: Archaeological Chemistry, Advances in Chemistry, 138, ACS Publications, 11-21.
- Gordon R. and Knopf R. (2007) Late horizon silver, copper, and tin from Machu Picchu, Peru. *Journal of Archaeological Science*, 34, 38-47.
- Gunter A.C. and Jett P. (1992) Ancient Iranian metalwork in the Arthur M. Sackler Gallery and the Freer Gallery of Art, Arthur M. Sackler Gallery and Freer Gallery of Art. Smithsonian Institution, Washington DC.
- Hughes M.J. (1986) Analysis of silver and gold items found in a hoard at Babylon. *Iran*, 24, 87-88.
- Ingo G.M., Balbi S., De Caro T., Fragalà I., Angelini E. and Bultrini G. (2006) Combined use of SEM-EDS, OM and XRD for the characterization of corrosion products grown on silver roman coins. Applied Physics A, Materials Science & Processing, 83, 493-497.
- Mongiatti A., Meeks N. and Simpson S.J. (2010) A gold four-horse model chariot from the Oxus Treasure: a fine illustration of Achaemenid goldwork. *The british Museum technical Research Bulletin*, 4, 27-38.
- Muscarella O.W. (1988) Bronze and Iron: Ancient Near Eastern Artifacts in The Metropolitan Museum of Art. Metropolitan Museum of Art, New York.
- Northover S.M. and Northover J.P. (2014) -Microstructures of ancient and modern cast silvercopper alloys. *Materials Characterization*, 90, 173-184
- Northover P., Northover S. and Wilson A. (2013) -Microstructures of ancient and historic silver. In: Metal 2013, 16-20 September 2013, Edinburgh, International Council of Museums ICOM-CC, 253-260.
- Oudbashi O., Shekofteh A., Makhzani S. and Siapoosh M. (2014) - Conservation of Metal Collection in Ebn-e Sina Museum, Hamedan, Iran: from Interventive to Preventive Approaches, Abstracts of International Conference YOCOCU 2014, Youth in the Conservation of Cultural Heritage, 28-30 May 2014, Agsu, Azerbaijan.
- Pigott V.C. (1990) Bronze; in Pre-Islamic Iran. In: Encyclopedia Iranica, (ed.): Yarshater E. Vol. IV, Routledge & kegan Paul, London and New York,

- 457-471.
- Pistofidis N., Vourlias G., Pavlidou E., Dilo T., Civici N., Stamati F., Gjongecaj S., Prifti I., Bilani O., Stergioudis G. and Polychroniadis E. K. (2006) On the comparative study of three silver coins of the III century B.C. minted in Korkyra, Dyrrachion and by the Illyrian king Monounios. *Applied Physics A, Materials Science & Processing*, 83, 637-642.
- Porada E. (1963) Iran Ancien: L'art De l'epoque pre'islamique, Albin Michel, Paris.
- Ross J.C. (2001) Gold I: in Pre-Islamic Persia.In: Encyclopaedia Iranica, XI, 1, 68-75.
- Schmitt R. (1983) Achaemenid Dynasty. In: Encyclopædia Iranica, I, 4, 414-426.
- Scott D.A. (1991) Metallography and Micro-structure of Ancient and Historic Metals, Getty Conservation Institute, Los Angeles.
- Scott D.A. (2010) Ancient Metals: Microstructure and Metallurgy, Vol. 1: principles and Practice, CSP, Conservation Science Press, Los Angeles.
- Shapur Shahbazi A. (2004) The Authoritative Guide to Persepolis, Sanaye Farhangi Iran (SAFIR), Tehran
- Simpson S.J., Cowell M.R. and La Niece S. (2010) -Achaemenid Silver, T.I. Jacks and the Mazandaran Connection. In: The World of Achaemenid Persia, History, Art and Society in Iran and the Ancient Near East, (Eds.): J. Curtis and S.J. Simpson, Proceedings of a Conference at the British Museum, 29th Sept.-1st Oct. 2005, I.B.Tauris, London, 429-442.
- Stierlin H. (2006) Splendors of the ancient Persia. Vercelli, Italy, White Star.
- Stronach D. (1986) Archaeology II: Median and Achaemenid, Encyclopaedia Iranica, II, 3, 288-296.
 Stronach D. (1978) - Pasargadae, Oxford University Press, Oxford.
- Stronach D. and Gopnik H. (2009) Pasargadae, Encyclopædia Iranica online, http://www.iranicaonline.org/articles/pasargadae.
- Taylor S.L. (2013) An Investigation of the Mechanical and Physical Properties of Copper-Silver Alloys and the Use of These Alloys in Pre-Colombian America, Bachelor Project, Massachusetts Institute of Technology (MIT).
- Vaníčková J., Děd J., Bartuška P., Drahokoupil J., Čerňanský M. and Lejček P. (2008) - Analysis of grain boundaries in an embrittled ancient silver necklace. Surface and Interface Analysis, 40, 454-457.

- Viljus A. and Viljus M. (2012) The Conservation of Early Post-Medieval Period Coins Found in Estonia. *Journal of Conservation and Museum Studies*, 10, 30-44.
- Wanhill R. (2013) Stress corrosion cracking in ancient silver. Studies in Conservation, 58, 41-49.
- Wanhill R.J.H. (2003) Brittle Archaeological Silver, A Fracture mechanisms and Mechanics Assessment. *Archaeometry*, 45, 625-636.

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