CrossMark

Metallurgical study on some Sasanian silver coins in Sistan Museum

Mohammad Mortazavi[1] · Sogand Naghavi[2] · Reza Khanjari[2] · Davoud Agha-Aligol[3]

Abstract Elemental analyses and microstructural studies of historical metal artifacts provide researchers with invaluable and priceless information about metal extraction technology and the procedure of creating artifacts. In addition, the information is helpful for knowing about the metallurgical processes of the artifacts. This study was conducted by a microscopic examination and elemental analyses of seven Sasanian silver coins preserved in the Sistan Anthropology Museum, Iran. For the purpose of this study, three methods were employed: first, the proton induced X-ray emission microanalysis (micro-PIXE), to determine the main and trace elements of the coins; second, scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS), to perform elemental analysis to identify impurities of the metal; and third, microstructural analysis of the coins which was carried out with an optical microscope (OM). The elemental analyses identified Ca, Cu, Ag, Au, and Pb in the coins. The high quantity of Ag in samples validated the application of advanced and accurate cupellation technology for refining silver and separating impurities from raw ore. The gold concentration in the coins indicated the use of non-galena ore for silver extraction. Additionally, the microstructural analyses of samples pointed to the application of thermo-mechanical processes on coins.

Keywords Silver coin · Sasanian period · Micro-PIXE · SEM-EDS · Microstructure

Introduction

Numismatics is a significant branch of archeology that addresses the identification of history, historical geography, religion(s), art, culture, economy, myths, clothing, traditions, and sometimes the architecture of each era (Hajivaliei et al. 2008; Tripathy et al. 2010). Meanwhile, numismatics can also help in studying some other aspects of arts and industry of people in ancient times. In this regard, the relevant uncertainties and questions can be addressed only through careful study and instrumental analyses (Kallithrakas-Kontos et al. 2000; Pistofidis et al. 2006). Precise identification and study of coinage process and main alloying elements in that era are important in revealing some valuable aspects of this art and industry (Bacharach and Gordus 1972). Among the useful instrumental techniques of analysis for this research, non-destructive instrumental analysis techniques such as optical microscopy, scanning electron microscopy (SEM), and proton induced X-ray emission microanalysis (micro-PIXE) were used.

In this study, seven Sasanian silver coins preserved in the Sistan Anthropology Museum were analyzed. Some surfaces of these coins were covered with corrosion products and contamination layers. So, the coins were cleaned for a clearer look of the images to study their figures and obtain accurate results.

✉ Sogand Naghavi
s_naghavi@uoz.ac.ir

Mohammad Mortazavi
m.mortazavi@live.com

Reza Khanjari
r_khanjari@uoz.ac.ir

Davoud Agha-Aligol
d_aligol@yahoo.com

[1] Faculty of Art Entrepreneurship and Tourism, Art University of Isfahan, P. O. Box 1744, Isfahan, Iran

[2] Faculty of Art and Architecture, University of Zabol, P. O. Box 98615-538, Zabol, Iran

[3] Van de Graaff Laboratory, Physics and Accelerators Research School, Nuclear Science & Technology Research Institute (NSTRI), P. O. Box 11365-3486, Tehran, Iran

Numismatic evidence showed that these coins belong to Piruz I (Fig. 1, Table 1).

The main objective of this study was to investigate the microstructure and alloying elements of the coins and to identify the relevant coinage processes. The investigation into the coins was done by means of microscopic and instrumental analysis techniques. In addition, the microstructural analyses were conducted to trace metallurgical and coinage processes through optical microscopy and scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS). The elemental analyses of the coins was carried out by proton-induced X-ray emission spectrometry to discover the alloys used in coinage and identify the impurities of samples.

Material and methods

To perform metallographic studies as well as phase and elemental analyses, sampling was done by a jewelry saw. In this process, small pieces (2 × 2 mm) were cut from broken edges of the coins and mounted in epoxy resin. Then, the surfaces of all samples were polished with emery paper (400–3000 grit). The final polish was performed by diamond paste of 1 and 3 μm. The microstructural analysis of samples was conducted by an optical microscope to investigate type, shape, and the distribution of phases and inclusions, using a BK-POL/BK-POLR optical microscope equipped with a Canon EOS Kiss X4 CCD camera and Breeze System image capture software. In this stage, pre- and post-etched samples were examined. For etching the samples, acidified potassium dichromate solution (10-ml sulfuric acid (98%) + 100-ml potassium dichromate, saturated $K_2Cr_2O_7$ in distilled water + 2-ml sodium chloride solution saturated in distilled water) was used (Scott 1991). Etching duration varied from 2 to 5 s. Microscopic assessment of samples was performed to investigate pre- and post-etched phases in metallic microstructures of the coins using SEM. In addition, the elemental analyses were carried out for obtaining the composition of alloys and existing

Table 1 Weight and diameter of examined Sasanian coins

	Weight (g)	Diameter (mm)
Coin 1	5.45	28.04
Coin 2	2.88	Immeasurable
Coin 3	3.45	29.08
Coin 4	3.14	27.5
Coin 5	3.27	26.50
Coin 6	2.82	27
Coin 7	2.97	29.6

impurities of the samples using SEM-EDS. This experiment was done in the Laboratory of Razi Applied Science Foundation in Tehran, using a MIRA3 field emission scanning electron microscope (TESCAN, Czech) equipped with energy dispersive X-ray spectroscopy (EDS) (RONTEC, Germany) and QUANTAX (QX2). Finally, the investigation of the alloy samples was done to identify main and trace elements, using micro-PIXE. The elemental analysis through PIXE is among the most common techniques for analyzing different historical artifacts (Linke et al. 2004; Stuart 2007). The three MV Van de Graaff accelerators at the Nuclear Science & Technology Research Institute in Atomic Energy Organization of Iran (AEOI) with scanning proton microprobe system manufactured by Oxford Instruments were used to perform micro-PIXE measurements (Grime and Watt 1988). Silver coins were analyzed in vacuum by using a beam of 2-MeV protons focused on a diameter less than 10 μm. The beam current was in the range of 30 to 50 pA. Characteristic X-rays were detected using a Si (Li) detector with an active area of 60 mm^2 positioned at an angle of 135° relative to the incident beam direction and an energy resolution of 150 eV for Fe-K_α. The samples were scanned by a beam over a maximum area of 2.5 mm × 2.5 mm. Digitized detector signals were recorded in event by event (list-mode) method with the instantaneous beam position using the OM-DAQ data acquisition system. In order to avoid any heterogeneity and obtain accurate fineness of silver coins, the core region of the analyzed area in Ag map distribution was chosen for extraction of the corresponding spectra. Then, the spectra of the micro-PIXE experiment was analyzed and evaluated by means of GUPIXWIN software (Campbell et al. 2010) which provided the elemental concentrations of the detected elements.

In order to check the validity of the micro-PIXE analysis and to confirm the accuracy of the measurements, one Euro coin (75% Cu, 25%Ni) and a pellet of copper-phosphorous-tin powder (86% Cu, 6.5% P, and 7.5% Sn) as standard targets were analyzed under the same condition. The evaluated composition of one Euro coin was 74.59% Cu and 24.80% Ni and copper-phosphorous-tin pellet was 84.90% Cu, 5.71% P, and 6.69% Sn. The results were in good agreement with the recommended values within 5% accuracy for major elements and, 5–10% accuracy for minor elements.


Fig. 1 Both sides of the Sasanian silver coins used in this study

Results and discussion

Elemental analysis

According to the PIXE results, silver was the main element of the coins' alloy. The silver content in all coins was higher than 90%, indicating their high purity like other Sasanian coins—particularly silver coins of Piruz with 90 to 98% silver amounts (Bacharach and Gordus 1972). In addition, low contents of Ca, Cu, Au, and Pb were observed in the alloys (Table 2).

The presence of these elements in silver coins can be used for the identification of the ores from which silver was extracted. At present, almost half of silver products are extracted from lead ores; however, the extraction of silver from lead ores was more widespread in ancient times (Hughes and Hall 1979). The technology of silver production from lead ore might date back to the beginning or middle of the third millennium BC (Meyers and Harper 1981). The silver metallurgy was developed out of lead smelting technology, and metal silver was extracted from argentiferous lead ores (Meyers 2003). In other words, silver metallurgy is derived from lead smelting technology, being extracted from cerussite ($PbCO_3$) and galena (PbS), using the cupellation process (Scott 2011). Cupellation results in silver purification and segregation of impurities such as copper, antimony, arsenic, tin, iron, zinc, and bismuth from argentiferous lead (Moorey 1994). Although, native silver, silver chloride and sulfide ores, and jarosite were mentioned as the sources of silver in ancient times (Craddock 2014; Scott 2011), it is generally believed that the majority of silver used in those times were extracted from argentiferous lead ores, specifically cerussite and probably galena (Giovannelli et al. 2005; Meyers and Harper 1981).

The gold content of coins was identified less than 1% (0.34–0.86%) (Table 2, Fig. 2). This amount of gold in the alloy used in silver artifacts is considered as natural impurity and can be used as an indicator of the source of the primary ore since it is not expected to be affected by smelting and cupellation (Constantinescu et al. 2005; Giovannelli et al. 2005; Kallithrakas-Kontos et al. 2000; Kantarelou et al. 2011; Meyers and Sayre 1971; Meyers et al. 1973). As mentioned
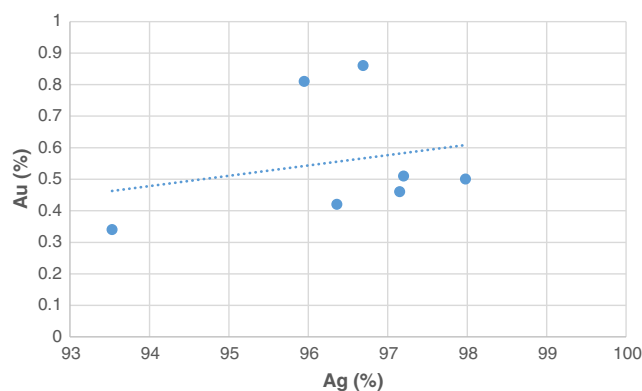
Fig. 2 Scatter plot of the gold vs. silver content in the analyzed coins by micro-PIXE

by Craddock (2009), any gold contained in the ore runs of with silver in cupellation process. In other words, due to the relatively similar amount of gold in the coins' alloy, the ores used for silver extraction could possibly have a similar mineralogy and chemistry. On the other hand, the gold content of the samples confirms the use of non-galena ores for the extraction of silver (Craddock 2014; Wood et al. 2017).

Geological surveys in Iran have shown the presence of great deposit of lead-bearing ores in different areas of the Iranian plateau (Meyers and Harper 1981). Therefore, it can be said that Sasanian silver workers have had access to primary ore for silver extraction. Nakhlak, Anguran, Duna, and Gorgab IV have been identified as the mines with traces of old mining mostly belong to late Sasanian-Early Islamic time (Nezafati and Pernicka 2012).

In a study of Sasanian silver coins by Bacharach and Gordus (1972), the same amount of gold in the alloy composition of their coins has also been reported. This amount of gold in the coins' alloy implied the use of argentiferous lead ores in silver extraction (Moorey 1994; Scott 2011). Similar results were obtained from a study of Sasanian silver objects by Meyers and Sayre (1971) which showed that the majority of objects made of metal alloys contained 92–96% silver, 3–7% copper, and 0.5–1% gold.

The analysis of silver coins in the present study showed the lead content of 0.13–1.17% in alloy composition. Having lead content in alloy compositions demonstrates the use of

Table 2 The results of elemental composition and standard deviations in weight percentage (wt%) for all elements determined in coins by micro-PIXE analysis

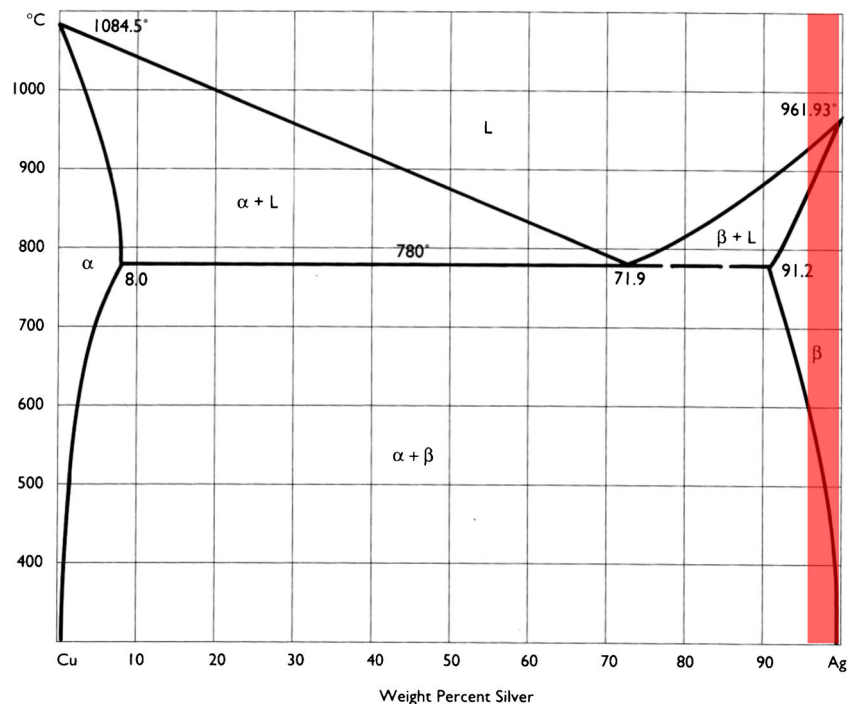|	Ag	Cu	Au	Pb	Ca
Coin 1	96.36 ± 5.84	2.19 ± 0.14	0.42 ± 0.16	0.45 ± 0.16	0.59 ± 0.09
Coin 2	97.98 ± 5.83	0.87 ± 0.10	0.50 ± 0.16	0.13 ± 0.05	0.52 ± 0.09
Coin 3	93.53 ± 6.54	4.47 ± 0.43	0.34 ± 0.07	0.78 ± 0.24	0.87 ± 0.14
Coin 4	95.95 ± 3.89	1.47 ± 0.06	0.81 ± 0.12	1.17 ± 0.17	0.60 ± 0.06
Coin 5	97.20 ± 5.63	1.31 ± 0.10	0.51 ± 0.17	0.34 ± 0.16	0.64 ± 0.09
Coin 6	96.69 ± 4.75	1.17 ± 0.07	0.86 ± 0.14	0.40 ± 0.13	0.89 ± 0.07
Coin 7	97.15 ± 4.35	1.04 ± 0.06	0.46 ± 0.11	0.71 ± 0.14	0.62 ± 0.06
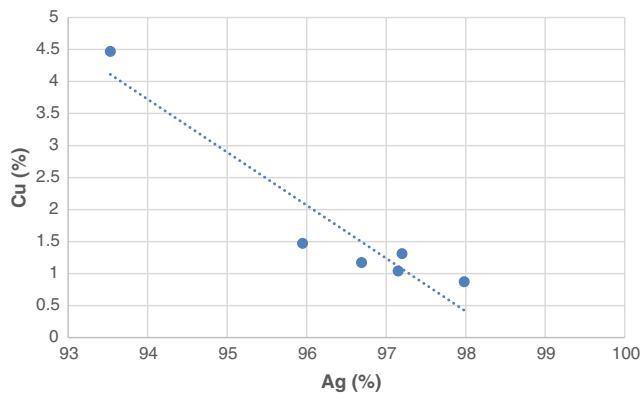
Fig. 3 Scatter plot of the copper vs. silver content in the analyzed coins by micro-PIXE

cupellation process in silver production (Craddock 2014; Scott 2011). Furthermore, the very low amount of lead in the coins' alloy suggests the use of a good silver refining process (Tripathy et al. 2010).

Alloy analysis of the coins showed that the copper content varied from 0.87 wt% in coin 2 to almost 4.47% in coin 3. The copper content in other coins varied from 1 to 2 wt% (Table 2, Fig. 3). For coin 3, it was higher than the level commonly known as impurity in metal silver (Meyers et al. 1973).

Silver artifacts often contain copper as an alloying element (Scott 1990). This element significantly increases the mechanical properties and the strength of silver (Meyers and Harper 1981; Meyers and Sayre 1971). The addition of 3–4% copper to silver was common in the ancient times (Scott 2011). This process resulted in the debased silver artifacts and was subsequently cost saving (Costa 2001; Scott 1991).

In addition to lead, copper, and gold, very low amounts of calcium were also identified in analyses which could be attributed to sedimentary layer on the surface of samples.

Microstructural analysis

The next stage in the analysis of metallurgical properties of metal artifacts was microstructural analysis of their metal body. This stage includes successive processes that ended in the identification of the metal artifacts' manufacturing processes. The microstructure of metal artifacts depends on different factors, such as manufacturing methods (hammering or casting), cooling rate, alloy's nature, and metal impurities used for their manufacturing (Bird and Hodges 1968). In addition, the microstructure of any historic metal object can illustrate the type of work done on it.

According to the results regarding the coins' alloy, copper was added to the silver as the main alloying element. Copper is one of the typical alloying elements in silver artifacts (Scott 1990). In historical artifacts, about 5–10% copper can been identified in combination with silver (Costa 2001). The addition of copper to silver was carried out in the past to make the silver alloy harder and reduce the used silver content, resulting in cost savings (Costa 2001; Scott 1991). This process has been generally traced back to the third millennium BC in the Mesopotamia (Philip and Rehren 1996).

The copper-silver alloy is a simple binary eutectic system in which the temperature and composition of the eutectic are 779 °C and 28.1 wt%, respectively (Hörz and Kallfass 2000). The maximum limit of the solubility of copper in silver at the

Fig. 4 The phase diagram of silver-copper alloys (Scott 1991). Range of the copper content of the silver coins is marked with *red color*

Fig. 5 The microstructure of coin 3 after etching where the jigsaw grain boundaries is clearly observed in the microstructure
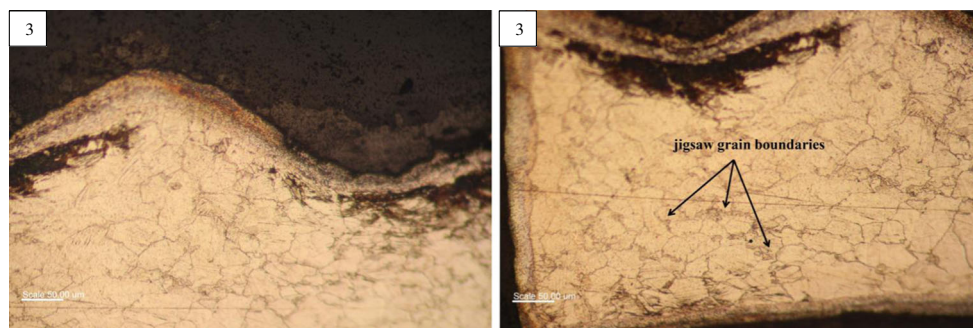

eutectic temperature is 8.27%. In addition, although the certain solubility of copper at room temperature is not defined, it's significantly lower than 1 wt% (Northover et al. 2013). In other words, copper solubility in silver decreases by reducing the temperature. This low amount of solubility results in supersaturated solid solution of copper. According to the silver-copper phase diagram (Fig. 4), a silver-rich structure exists in the supersaturated state in which copper concentration is greater than its solubility limit at room temperature. The solution of copper in the silver grains is therefore occurring in a metastable state which can be precipitated slowly with time at the grain boundaries (Scott 1991).

The PIXE analysis of the coins identified 1–4 wt% copper. The status of this group of coins based on their copper content is presented in Fig. 4. According to the diagram, copper content in some of these coins is higher than the solubility limit of copper in silver at room temperature. As a result, there is a chance of discontinuous precipitation of copper at the grain boundaries which refers to precipitates laid down at the boundaries, often by a process of aging or exsolution of

metastable phases (Scott 1991). An example of this phenomenon was observed in the coins under investigation.

The precipitation of copper at the grain boundaries smooths out the boundaries' facets by turning them into jigsaw-like structures with irregular shapes (Scott 1990, 1991; Wanhill 2011). An obvious example of this state is presented by the metallographic images of coin 3 (Fig. 5) in which grain boundaries have a jigsaw appearance. Considering the copper content of this coin (4.47 wt%), there is a possibility of copper precipitation. Moreover, quenching the high temperature silver-copper alloy is considered as the main cause of this phenomenon (Northover et al. 2013). In this state, the solid solution of copper is firstly formed in silver-rich β phase, while quenching prevents copper from segregating and reaching a stable condition during solidification. However, since the dissolution of copper in silver is very low in solid state at room temperature, grains get into a metastable state and the alloying elements tend to segregate (Costa 2001). As a result, copper slowly and in the long term begins to separate out and lay down at grain boundaries.
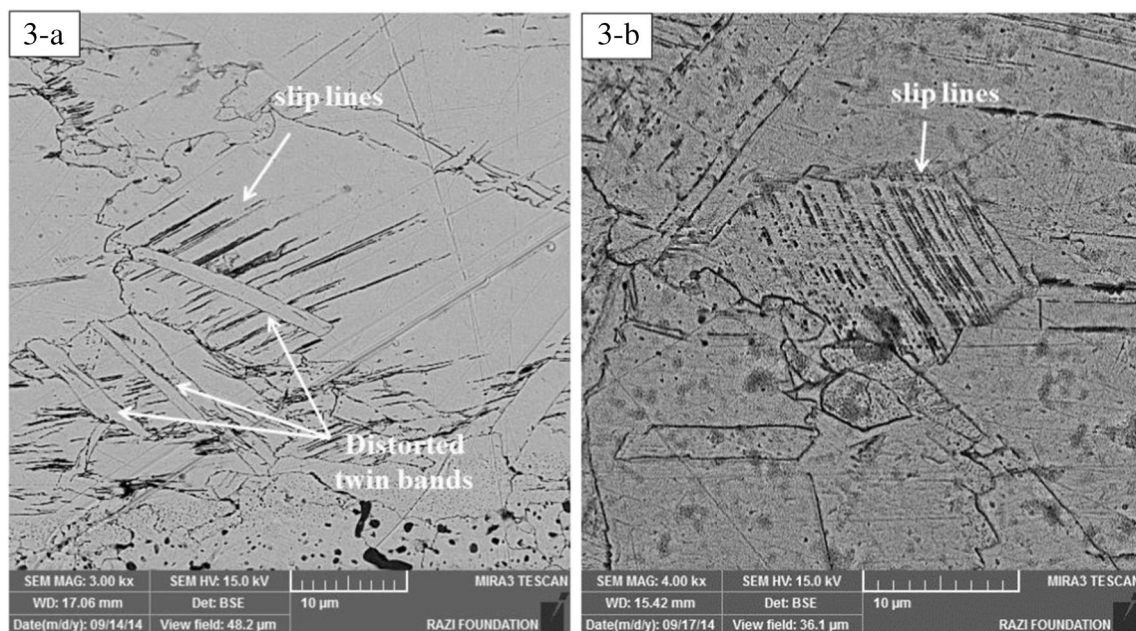
Fig. 6 SEM-BSE image of microstructure of coin 3 showing slip lines and deformed twin bands in the grains
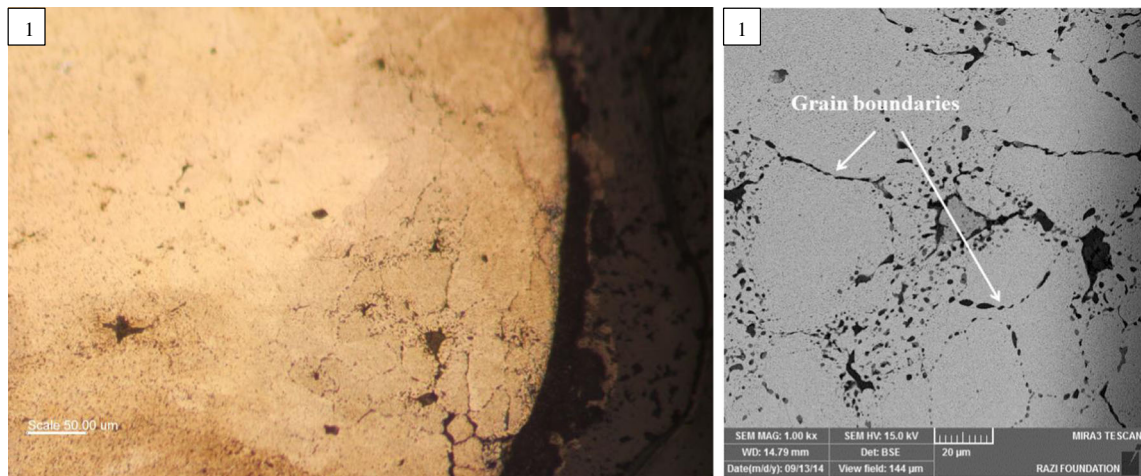
Fig. 7 OM and SEM-BSE images of the microstructure of coin 1 where silver-rich β phase and copper-rich α grain boundaries can be seen

On the other hand, since the discontinuous precipitation of copper is a long-term process, the jigsaw pattern of grain boundaries caused by copper precipitation can be used to establish the authenticity of ancient silver artifacts (Scott 1990). Therefore, the microstructure of this sample not only determines the metallurgical processes but also establishes the antiquity and authenticity of it. Nevertheless, the segregation of copper may occur during the final annealing of silver-copper alloy (Wanhill 2011). In addition, Northover et al. (2013) showed that copper precipitation at grain boundaries might also occur due to mechanical and thermal operations; therefore, it is not clear whether it has happened in the long term or during the production process.

SEM investigation of coin 3 revealed other aspects of its microstructural properties. SEM-BSE images illustrated not only the serrated pattern of grain boundaries but also the presence of strain and twin lines in the grains (Fig. 6). The presence of slip bands in the microstructure demonstrates that this coin was cold-worked (Pistofidis et al. 2006). In other words, cold-working has resulted in the rearrangement of atomic planes which causes the planes of atoms to slip. The slip can be seen in a series of parallel or intersecting lines in the microstructure. These lines are called slip bands or strain lines (Scott 1991). In addition, the twin bands can be seen in SEM images of coin 3.

The twin bands occur in microstructures of FCC metals, such as silver-copper alloy, which were firstly cold-worked and then annealed or hot-worked (Frame 2010; Mortazavi et al. 2011; Pistofidis et al. 2006). However, twin bands in this coin are not straight and are slightly curved which suggests

Fig. 8 Metallographic images of coins 2, 4, 6, and 7 showing recrystallized and twinned grains
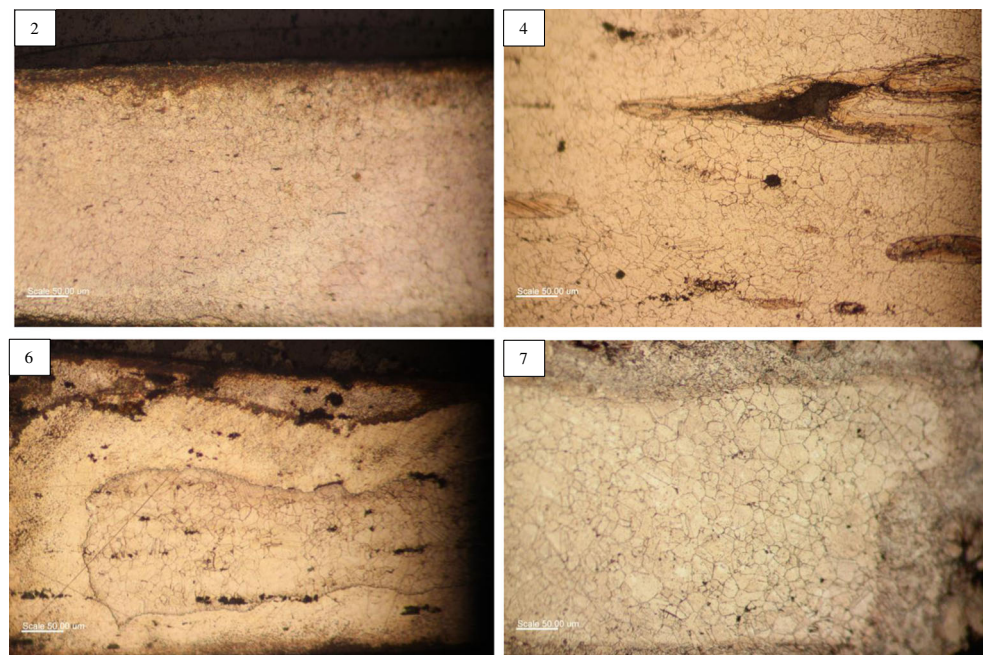
that the coin was cold-worked after the final annealing (Scott 1991). The slip lines remained from the final hammering can be seen in its microstructure.

Coin 1 has a different structure (Fig. 7). It can be seen that the microstructure is composed of two phases. The silver-rich β phase which forms the overall structure is segregated by a dark region in the grain boundaries. Coin 1 contained the greatest amount of copper secondary to coin 3 (2.19 wt% copper was measured in the alloy composition of this coin).

The structure of this coin can be explained on the basis of the copper content and silver-copper phase diagram. Since the copper content is less than 8% in this coin, its alloy is categorized as hypoeutectic. Accordingly, a silver-rich β phase is firstly formed upon cooling from the melt (Costa 2001), and as a result, the copper content in the molten alloy increases with segregation of β-phase from the melt. However, this amount of copper is less than the copper content required for the formation of the eutectic composition. When temperature
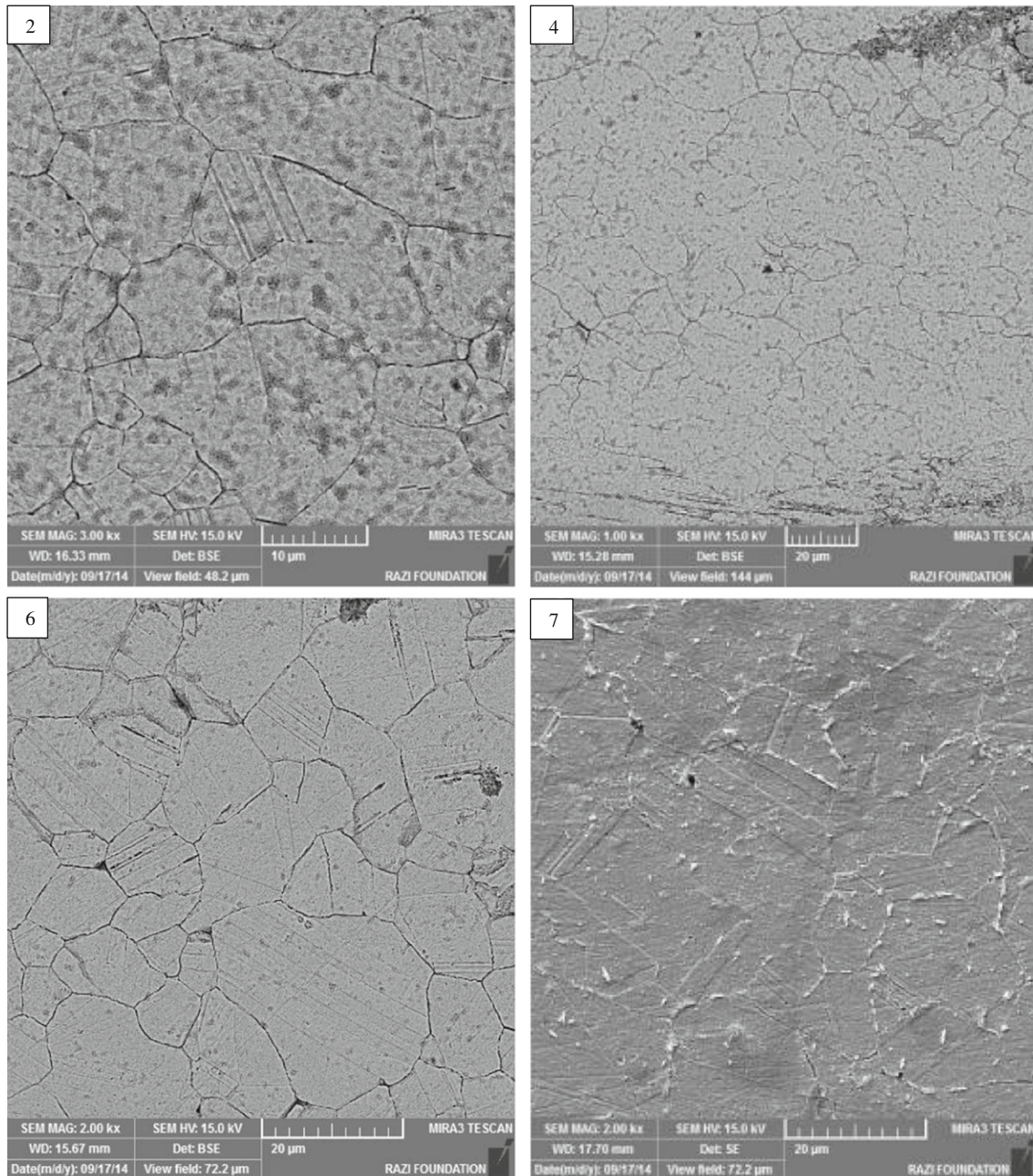
Fig. 9 SEM-SE and SEM-BSE images of the microstructure of Sasanian silver coins 2, 4, 6, and 7. *Top left*: shows a BSE image of the microstructure of coin 2 after etching where recrystallized and twinned structure can be seen. *Top right*: shows the recrystallized structure of the coin 4. *Bottom left*: shows the recrystallized microstructure of the coin 6 with twin bands. *Bottom right*: shows SEM image of the coin 7 with recrystallized grains and twin bands

reaches the solidus line, the melt converts to the β phase (Scott 1991). With further cooling, the temperature reaches the solvus, resulting in the transformation of β phase into copper-rich α and β phases which is associated with the precipitation of copper-rich α phase in the primary grain boundaries of β phase (Pistofidis et al. 2006). Therefore, the primary piece of this coin was firstly casted and then minted. Nevertheless, minting evidences such as slip bands were not observed in this coin.

Microscopic studies of coins 2, 4, 6, and 7 showed that they had similar microstructures (Fig. 8). Structure of these coins included recrystallized equiaxed grains with twin bands. This structure suggests that the coins were hammered and annealed (Mortazavi et al. 2011).

In FCC metals, the formation of annealed twins is observed when the metal is hot-worked, or when the cold-worked metal is annealed (Pistofidis et al. 2006). On the other hand, smaller grain sizes in these coins, as compared to other coins, suggest the application of greater amount of works on them (Chase 1968; Scott 1991).

Due to the smaller grain sizes in these coins, their microstructures were studied with SEM. The study showed straight twin bands in coins 2, 6, and 7, whereas, the twin bands in coin 4 were partially deformed (Fig. 9).

The straight twin bands in coins 2, 6, and 7 point to the application of annealing after or during hammering operation (Frame 2010). On the other hand, bent twins in coin 4 suggest some cold-working after the final annealing (Scott 1991).

The metallographic and microstructural analyses of coin 5 showed worked grain structures, containing many slip bands across the surface of samples as well as deformed twin lines (Fig. 10). The presence of strain bands in the microstructure suggests cold-working on the coin (Pistofidis et al. 2006).

There are two prominent mechanisms of plastic deformation in metals, namely slip and twinning (Avner 1964). Results of the crystalline planes' slipping can be observed in the form of fine parallel or intersecting lines in metal microstructures.

In coin 5, the slip lines are seen in many grains in the form of fine parallel or intersecting lines. On the other hand, the curved and deformed twin bands can be seen in metallographic images of this coin. In this regard, coin 5 is similar to coin 3, except that it has straight grain boundaries. The curved twin bands in this coin suggest the application of cold-work after the final annealing operation (Scott 1991). In other words, different hammering and annealing operations along with cold-working at the final stage were carried out for metal formation.

In addition, coin 5 has a greater grain structure than other coins which may be due to over-annealing during heating treatment. A lengthy silver alloy annealing may lead to growth of the grains and recrystallization of the alloy structure. These grains are mechanically weak and generally avoided in new mechanical operations (Scott 1990). Regarding the existence of slip lines, the fracture along the grain boundaries seen in a part of the sample section (Fig. 11) may have occurred due to the application of cold-work operation on the coin which was mechanically weakened by over-annealing. Furthermore, the effects of mechanical treatment and work-hardening on metals should be considered. In other words, cold-work operation makes metals harder and less flexible (Avner 1964). The hardening process is continued by further hammering to the point that more hammering operation is no longer possible. In this state, the metal is work-hardened and cold-working of these metals leads to fracture and crack. However, the former is more likely to happen due to the large size and recrystallized shape of the grains.

Fig. 10 Metallographic image of coin 5 showing slip lines in the form of fine parallel or intersecting lines with slightly curved twin bands in the microstructure after etching with acidified potassium dichromate
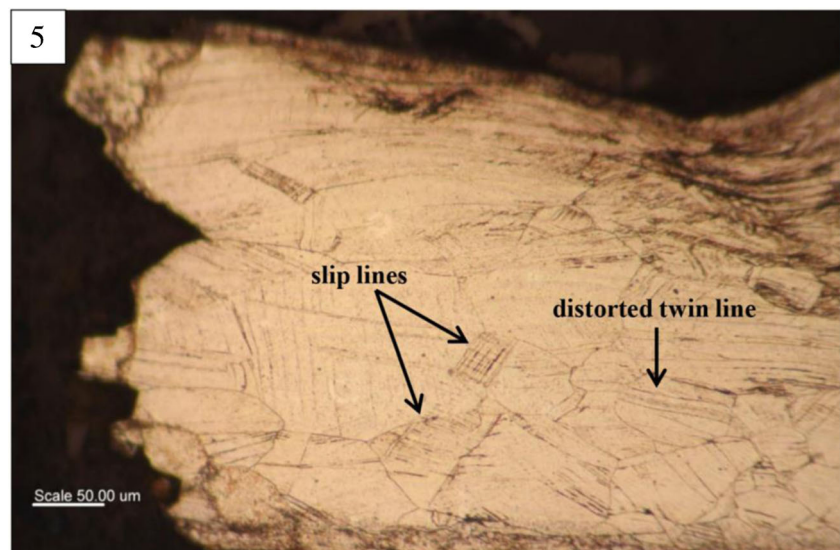
Fig. 11 Metallographic image of coin 5 showing intergranular fracture of the grains
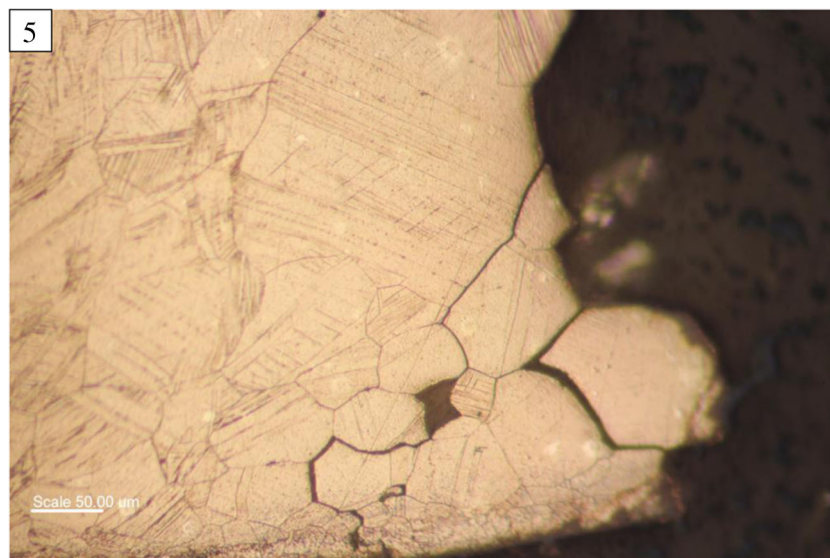
Conclusion

Results of this study improved our knowledge of the metallurgical technology in Sasanian period. The high purity of silver in the coins clearly points to metallurgical technologies used for silver refining and extracting in Sasanian era. In other words, there was a precise control over silver purification in that era. The high silver content (>90 wt%) in all coins indicates the precise and controlled application of cupellation operation to refine silver and segregate other impurities from the primary ores. Moreover, the gold content in the alloys suggests that the non-galena ores were used for silver extraction. On the other hand, relatively equal gold content in all coins suggests that the ores used for silver extraction had a similar mineralogy and chemistry. Microstructural analysis of samples validated the authenticity and antiquity of them by providing credible evidences such as copper precipitation in grain boundaries and formation of the irregular jigsaw appearance of grain boundaries in coin 3 with a greater copper content in the alloy. Evidences of mechanical operations along with annealing treatment were observed in other samples which may suggest pre-heating of the primary silver before minting.

References

Avner SH (1964) Introduction to physical metallurgy. McGraw-Hill, New York

Bacharach JL, Gordus AA (1972) The purity of Sasanian silver coins: an introduction. J Am Orient Soc 92(2):280–283

Bird V, Hodges H (1968) A metallurgical examination of two early iron swords from Luristan. Stud Conserv 13:215–223

Campbell J, Boyd N, Grassi N, Bonnick P, Maxwell J (2010) The Guelph PIXE software package IV. Nucl Instrum Methods Phys Res, Sect B 268:3356–3363

Chase WT (1968) The technical examination of two Sasanian silver plates. Ars Orientalis 75–93

Constantinescu B, Bugoi R, Oberlander-Tarnoveanu E, Parvan K (2005) Some considerations on X-ray fluorescence use in museum measurements—the case of medieval silver coins. Romanian Reports in Physics 57:1021

Costa V (2001) The deterioration of silver alloys and some aspects of their conservation. Stud Conserv 46:18–34

Craddock P (2009) Scientific investigation of copies, fakes and forgeries. Butterworth-Heinemann, Oxford

Craddock P (2014) Production of silver across the ancient world. ISIJ Int 54:1085–1092

Frame L (2010) Metallurgical investigations at Godin Tepe, Iran. Part I: the metal finds. J Archaeol Sci 37:1700–1715

Giovannelli G, Natali S, Bozzini B, Siciliano A, Sarcinelli G, Vitale R (2005) Microstructural characterization of early western Greek incuse coins. Archaeometry 47:817–833

Grime G, Watt F (1988) Focusing protons and light ions to micron and submicron dimensions. Nucl Instrum Methods Phys Res, Sect B 30: 227–234

Hajivaliei M, Mohammadifar Y, Ghiyasi K, Jaleh B, Lamehi-Rachti M, Oliaiy P (2008) Application of PIXE to study ancient Iranian silver coins. Nucl Instrum Methods Phys Res, Sect B 266:1578–1582

Hörz G, Kallfass M (2000) The treasure of gold and silver artifacts from the Royal Tombs of Sipán, Peru—a study on the Moche metalworking techniques. Mater Charact 45:391–419

Hughes MJ, Hall J (1979) X-ray fluorescence analysis of late Roman and Sassanian silver plate. J Archaeol Sci 6:321–344

Kallithrakas-Kontos N, Katsanos A, Touratsoglou J (2000) Trace element analysis of Alexander the Great's silver tetradrachms minted in Macedonia. Nucl Instrum Methods Phys Res, Sect B 171:342–349

Kantarelou V, Ager FG, Eugenidou CF, Andreou A, Kontou E, Katsikosta N, Respaldiza MA, Serafin P, Sokaras D, Zarkadas C, Polikreti K, Karydas AG (2011) X-ray fluorescence analytical criteria to assess the fineness of ancient silver coins: application on Ptolemaic coinage. Spectrochimica Acta Part B: Atomic spectroscopy 66:681–690

Linke R, Sehreiner M, Demortier G, Alram M, Winter H (2004) The provenance of medieval silver coins: analysis with EDXRF, SEM/EDX and PIXE. Compr Anal Chem 42:605–633

Meyers P (2003) Production of silver in antiquity: ore types identified based upon elemental compositions of ancient silver artifacts. In: patterns and process: a Festschrift in Honor of Dr. Edward V. Sayre, p 271–288

Meyers P, Harper P (1981) Silver vessels of the Sasanian period. I: the Royal Imagery New York

Meyers P, Sayre EV (1971) The determination of trace elements in ancient silver objects by thermal neutron activation analysis. Bulletin of the American Group International Institute for Conservation of Historic and Artistic Works 11:29–33

Meyers P, Van Zelst L, Sayre EV (1973) Determination of major components and trace elements in ancient silver by thermal neutron activation analysis. J Radioanal Chem 16:67–78

Moorey P (1994) Ancient Mesopotamian materials and industries? The archaeological evidence. Clarendon Press, Oxford

Mortazavi M, Salehi Kakhki A, Golozar MA, Tala'i H (2011) Preliminary metallurgical investigation of copper-based artifacts at Tepe Sagzabad in Qazvin Plain, Iran (1500–800 BC). Iranian Journal of Archaeological Studies 1:49–59

Nezafati N, Pernicka E (2012) Early silver production in Iran. Iranian Archaeology 3:38–45

Northover P, Northover S, Wilson A (2013) Microstructures of ancient and historic silver

Philip G, Rehren T (1996) Fourth millennium BC silver from Tell esh-Shuna, Jordan: archaeometallurgical investigation and some thoughts on ceramic skeuomorphs. Oxf J Archaeol 15:129–150

Pistofidis N, Vourlias G, Pavlidou E, Dilo T, Civici T, Stamati F, Gjongecaj S, Prifti I, Bilani O, Stergioudis G (2006) On the comparative study of three silver coins of the IIIrd century BC minted in Korkyra, Dyrrachion and by the Illyrian king Monounios. Applied Physics A 83:637–642

Scott DA (1990) A technical and analytical study of two silver plates in the collection of the J. Paul Getty Museum. The J Paul Getty Museum Journal 18:33–52

Scott D (1991) Metallography and microstructure of ancient and historic metals. Los Angeles, The J. Paul Getty Trust, 1991a

Scott DA (2011) Ancient metals: microstructure and metallurgy. Vol 1. Lulu. com

Stuart BH (2007) Analytical techniques in materials conservation. John Wiley & Sons, New York

Tripathy B, Rautray TR, Rautray A, Vijayan V (2010) Elemental analysis of silver coins by PIXE technique. Appl Radiat Isot 68:454–458

Wanhill R (2011) Case histories of ancient silver embrittlement. J Fail Anal Prev 11:178–185

Wood JR, Charlton MF, Murillo-Barroso M, Martinón-Torres M (2017) Iridium to provenance ancient silver. J Archaeol Sci 81:1–12