Metallurgical and Materials Engineering *Research paper*
Association of Metallurgical Engineers of Serbia AMES *https://doi.org/10.30544/524*

METALLURGICAL INVESTIGATIONS OF INDO-SASANIAN COPPER-SILVER ALLOY COINS OF GURJARA-PRATIHARAS DYNASTY

Meenakshi Malsure[1], Preeti Verma[2], Manager Singh Rajdeo[2]*

[1]Department of Conservation, National Museum Institute, Janpath, New Delhi-110011, India
[2]National Research Laboratory for Conservation of Cultural Property, Aliganj Lucknow-226024, India

Received 23.06.2020
Accepted 21.10.2020

Abstract

Five Indo-Sasanian copper-silver alloy coins were examined to determine the chemical composition and fabrication route. Based on iconography, the investigated coins were dated in the range 8th to 9th century CE. The chemical composition of the coins confirmed that the coins were made of copper-silver alloy. The percentage of silver was found to be in the range from 14 wt.% to 16 wt.%, and other elements iron and lead were present as impurities. There was no significant difference in the chemical composition from the surface to the center. Chlorine was detected in the localized green corrosion, which confirms the presence of active corrosion, and coins must be conserved by giving proper conservation treatment. The formation of unusual active corrosion compounds i.e. paratacamite was identified by the XRD, and this may be formed due to the exposure of coins to river water and soil. Optical microscopy revealed the dendritic and dual-phase structure, and the presence of dendrite showed that the coins were manufactured by the casting. It was confirmed from the optical microscopy that coins were not subjected to heat treatment and deformation. The microstructure consists of dual phases, in which the white phase is silver-rich, and the black phase is rich in copper. The morphology and chemical composition of the corrosion compound formed on the surface of the coins mainly indicated the formation of copper oxide with different morphology.

Keywords: Indo-Sasanian;Copper-silver coins; Dendrite; Paratacamite; Casting; Corrosion.

[*]Corresponding author: Manager Rajdeo Singh, *m_singh_asi@yahoo.com*

Introduction

The Sasanian Empire was established by Ardashir in 224 AD and lasted until the middle of the 7th century. It was one of the most prosperous and dominant states in the ancient world [1]. Different types of metal coinage such as silver, gold, copper, and silver-copper were used during the Sasanian Empire [2, 3]. Ancient coins are important archaeological objects and these may provide valuable information such as manufacturing technology, provenance as well as politics, and economics of that time [4]. The differences in design, value, metal, shape, and technology of coins may be due to the different rulers, art, and fashion. The typology, mint, denomination, and chemical composition of the Sasanian coins were studied under the project entitled "Sylloge Nummorum Sasanidarum" [5, 6]. The chemical composition of the Sasanian silver coins was determined using various non-destructive techniques such as X-ray fluorescence (XRF), proton-induced X-ray emission (PIXE), scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) [1-2, 5-10], and percentage composition was used to explain the locations and identification of coin mines [1,8]. Mercury was observed on the surface of the silver coins of the emperor Khusro II (591–628) [7]. The presence of gold in the silver coins indicated the use of non-galena ore for silver extraction, and microstructural analyses of samples pointed to the application of thermo-mechanical processes on coins [9]. The chemical composition and microstructure of the silver-copper coins were examined using SEM-EDS and optical microscopy [10]. The present investigation deals with Indo-Sasanian coins. Indo-Sasanian coins were derived from the Sasanian coins and probably transmitted to India by the Alchon Huns, and these were mainly used in the areas of Gujarat and Rajasthan in western India and in the Gangetic region, from the 6th century to the 12th century CE [11-12].

It is quite obvious from the existing literature that most of the studies were focused on the determination of the elemental composition of Sasanian silver coins. The literature related to the Indo-Sasanian copper-silver coins is very scarce. It is practically difficult or impossible to give precise information about the fabrication route of the coins based on chemical composition and non-destructive tests. However, micro-destructive metallurgical examination with a very small sample without affecting the aesthetic value of the object can give complete information about the manufacturing techniques. In the present investigation, our objectives are to determine the chemical composition and microstructural analysis to understand the manufacturing procedure and corrosion behavior of the investigated Indo-Sasanian coins.

These coins were collected from the river bed of the Chambal River in the Malwa region of the central Indian state Madhya Pradesh, India, and geographic location is shown in figure 1. It is a volcanic plateau that is located in the western-central portion of India. It extends a small portion of the Indian states of Madhya Pradesh, Maharashtra, and Rajasthan.

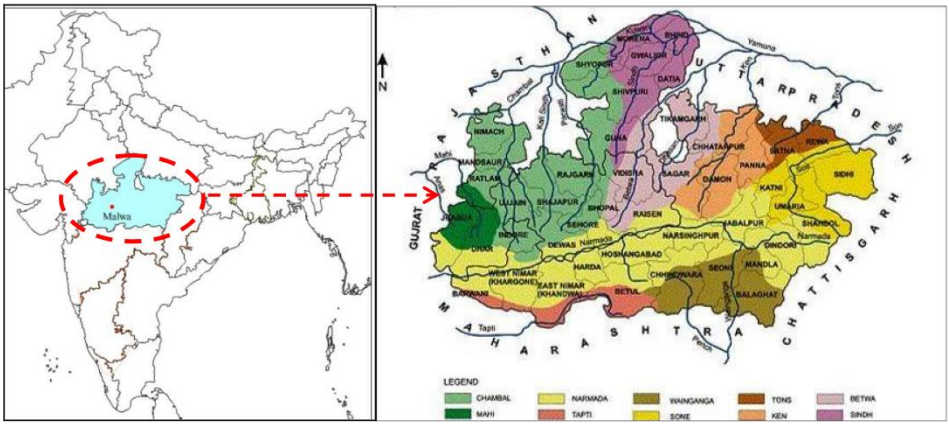


Fig. 1. (a) Geographic location of Malwa region shown in modern India map & (b) magnified view of Malwa.

This plateau has an average height of about 500 meters from the mean sea level. In ancient India, this region has come under the Avanti Mahajanpad, daspursasanian dynasty Gurjara-Pratiharas.

Material and Methods

The investigated Indo-Sasanian coins were sourced from the private collection of the corresponding author, and five representative coins were selected for this study. It may be seen from figure 2 that the coins were cemented to each other. Before the detailed photography and scientific investigation, coins were separated from each other by gently washing with distilled water and subsequently washed with acetone to remove the soil contamination present on the surface of the coins.

Fig. 2. The coins were found cemented to each other at the river bed.

The typical photomicrographs of obverse and reverse sides for two coins are shown in figure 3. It may be seen from the figures that inscriptions are present on both sides of the coins; however, the surface of some coins seems to be flat. It is important to mention that coins were not subjected to any other chemical treatment. The dimension of the coins, such as diameter and weight, were measured and displayed in Table 1.

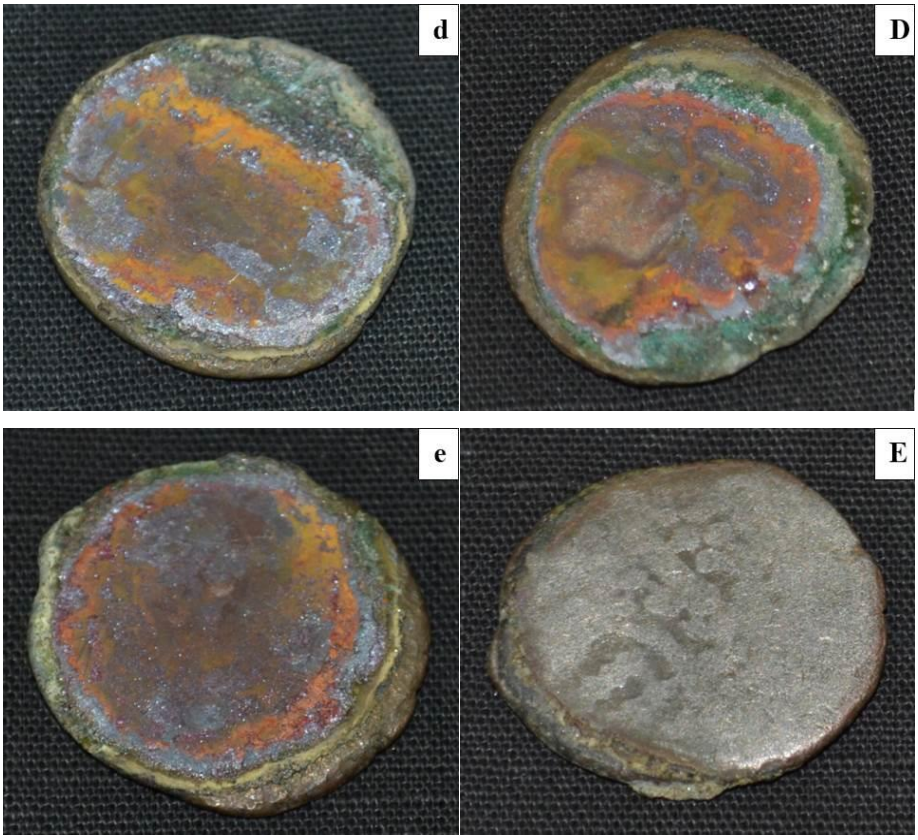


Fig. 3: Photographs showing the obverse and reverse side of all the investigated coins (a, A) Coin No 1, (b, B) Coin No 2, (c, C) Coin No 3, (d, D) Coin 4, and (e, E) Coin 5.

Table 1. The average diameter and weight of the studied coins.

Coin No	Average diameter (in cm)	Weight (in g)
1	1.98	3.23
2	2.00	3.03
3	2.00	3.35
4	1.95	2.89
5	1.97	3.02

All coins were analyzed by energy dispersive X-ray fluorescence (EDXRF) using Rigaku spectrometer NEX DE VS to determine the chemical composition of the coins. This instrument non-destructively analyzes the elements from sodium to uranium. The maximum operating voltage and current of the X-ray tube are 60 kV and 1mA, respectively. QuantEZ analytical software was used for the quantitative analysis of the elements, and quantification was achieved using the fundamental parameter based on reference materials. The certified and measured value of the reference material with lower limit detection (LLD) is given in table. 2. In order to determine the chemical

composition of the localized corrosion/incrustation present on the surface of the coins, a portable micro-X-ray fluorescence spectrometer (Model: Artax 200) was used, and the spectrum was recorded at 50kV with a live time of 30 seconds. The crystalline phases present on the surface of the coins were identified by the HR-XRD (Model: Panalytical). Coins were analyzed non-destructively for XRD analysis. XRD data were collected for the 2θ range from 5 to 110 ° with a scan rate of 2 °/min, and peak identification was carried out using the JCPDS software. To investigate the microstructure of the coins, very small samples were sectioned using a slow-speed diamond cutter. These samples were cold mounted in epoxy resin with a setting time of 30 min and mechanically polished on the different grades of silica carbide/emery papers from 400 to 2000 and subsequently, cloth polished with alumina paste to get the mirror finished. Samples were chemically etched with a solution of 100 ml distilled water, 30 ml hydrochloric acid, and 10 g ferric chloride to reveal the microstructure. Optical micrographs were recorded in various areas and at different magnifications using an optical microscope (Model: Leica Image analyzer). The microhardness of the coins was determined by applying a load of 25 g with a dwell time of 10 s using Vickers microhardness tester. Mounting was removed from the samples to avoid the charging effect in a scanning electron microscope. The chemical composition of the microstructural phase was determined using SEM-EDS (Model: FEI Jeol). The surface morphology and chemical composition of the corrosion compounds formed on the surface of the coins were also determined using SEM-EDS.

Table 2. The certified and measured value of the reference material 33X GM8 (Gun Metal).

Element	Certified	Measured	LLD
Cu	83.64	83.3	
Ag	0.1018	0.102	0.0012
Pb	6.21	6.27	0.0059
Zn	5.71	5.73	0.0069
Sn	4.03	4.24	0.0077
Ni	0.149	0.151	0.0059
Fe	0.033	0.0350	0.0046
As	0.0114	0.0115	0.0004
S	0.0083	0.0199	0.0003
P	0.0062	0.0061	<0.0001
Co	0.0222	0.0235	0.0037
Sb	0.0237	0.0237	0.0013
Bi	0.062	0.0557	0.0024

Results and Discussion

Macroscopic Examination

A critical examination of the inscription reveals that the crown posed face of the king towards the right on the obverse side. However, the fire altar flanked by vertical strings of diamond-shaped beads, and deities at each side of the fire alter are present on the reverse side (Fig. 2). It may be clearly understood from the inscription that the investigated coins are Indo-Sasanian coins. Stylizing of the Indo-Sasanian coins was

mainly derived from the Sasanian coins in a geometric fashion among the Gujaras, Pratiharas, Chaulukya-Paramara&Palas, and this design was probably transmitted to India by the Alchon Huns and issued various types of coins on the pattern of the Sasanian Empire. Physical observation of the coins confirms the Indo-Sasanian variety of the 8th-9th century CE, which is being affiliated to the rulers of north India, including Pala and Pratihara rulers. The investigated coins belong to the Gurjara-Pratiharas dynasty. These types of coinages were used for several centuries in India, and progressive degradation was noticed in the stylization of the original Sasanian design. It varied from one region to another region and lasted until the 11th-12th century CE in Gujarat, Rajasthan, and even up to the middle Gangetic plain [11]. In a typical Sasanian coin, the face of the king on the obverse side is highly simplified and geometric, and a fire altar with or without the two attendants appears as a geometrical motif on the reverse side of the coin [11, 12]. These coins were mainly traded in some parts of Indian states of Gujarat, Rajasthan, and Madhya Pradesh. It may also be seen from figure 3 that in some coins, inscriptions are not clearly visible due to the deposition of incrustation/corrosion on the surface. Inscriptions may be visible after giving proper conservation treatment.

It is observed from Table 1 that the average diameter of the coin is approximately similar; however, there is a slight variation in the weight of the coins. The variation in the weight of the coins may be due to the removal of material by continuous use of the coins, which may result in a slight reduction in the weight or increase in the weight due to the formation of corrosion compound on the surface of the coins. The formation of a uniform grey color layer on the surface is seen in coin no 1; however, in some coins, localized incrustation/corrosion of green and reddish-brown pigment was observed. The weight of the silver Sasanian coins was reported in the literature as nearly 4 g [1]; on the other hand, *Ham-Meert et al.* examined the lead coins of various sizes, and the weight of the coins was found to be in the range from 1 g to 16 g [3]. It may be understood that the weight of the investigated Indo-Sasanian coins is lower in comparison to the silver and lead Sasanian coins. The weight difference may be due to the lower density of the copper in comparison to the lead and silver and the difference in the size of the coins.

Chemical Composition

Elemental analysis

The analysis of the elemental composition of ancient coins is of considerable interest because the economic state of the dynasty can be inferred from the composition. The average value of the elemental composition of all the coins in wt.% is given in Table 3. The percentage of silver was found to be in the range of ≈14 to 16 wt. %. The XRF spectra were recorded for both obverse, and reverse side of the coins and percentage composition was found to be similar. It may be seen from the table that copper and silver are the main alloying element, and the presence of iron and lead was detected in traces. The presence of chlorine peak was observed in green pigment present on the surface in the spectrum recorded by the portable XRF and sulfur was also detected at some places. However, the intensity of peaks corresponding to sulfur and chlorine were very low in comparison to the other alloying elements. The percentage calculated from the software for chlorine and sulfur is below the detection limit for the quantitative analysis by μ-XRF.

Table 3. The elemental composition of the coins in wt. %.

Element	Coin No					
	1	2	3	4	5	LLD
Cu	83.4	83.5	83.7	82.1	83.2	0.0022
Ag	15.3	15.0	14.7	16.3	15.3	0.0045
Pb	0.9	1.4	1.3	1.4	1.1	0.0213
Fe	0.3	0.1	0.1	0.2	0.2	0.0106

Thus, it may be concluded from the elemental composition that coins were made up of the copper-silver alloy, and lead and iron were present as impurities. The study of the Saasnian silver coins shows a strong negative correlation between Ag and Cu; the more the Ag content, the less will be that of Cu. Moreover, a negative correlation between Ag and Pb can also be seen [1]. In general, lead is added to the copper alloy to increase the fluidity of the molten material [5]. However, the concentration of lead in the investigated coins is very low (approximately 1%). This might not be added intentionally for the making of the coins, and a lower percentage of lead suggest that the use of the cupellation process in silver production [13]. It is well known that iron oxide was deliberately added as a fluxing agent in the pyrometallurgical extraction of copper, tin, and lead from their ores. Iron in significant quantities frequently occurs in Iron Age and pre-Iron Age copper that has been formally recognized. The presence of iron in Iron Age copper may be attributed to various factors, such as the use of iron manipulative tools and stirring rods in remelt operations. [14, 15]. The high iron content in copper suggests the possibility of the use of unrefined copper. The general level of iron in the early copper or primitive copper (around 0.05%)is much the same everywhere, be it from Egypt, Britain, India, and the same is true of the enhanced levels associated with more advanced copper production where an average level of around 0.3% is fairly typical [10, 16]. Thus, it may be understood that the iron might have entered in the copper during the smelting process.

XRD Analysis

XRD pattern for the coin no 3 and 5 is shown in figure 4. It may be seen from the figure that there is no change in the peak position in both coins, and only a slight variation in the intensity of the peak may be noticed. All peaks were analyzed with the JCPDS software to determine the compound, and the presence of Cu, Ag, Ag_2S, Cu_2O, and paratacamite ($Cu_2(OH)_3Cl$) was confirmed. Thus, it may be evidenced that a similar compound was observed in both coins.

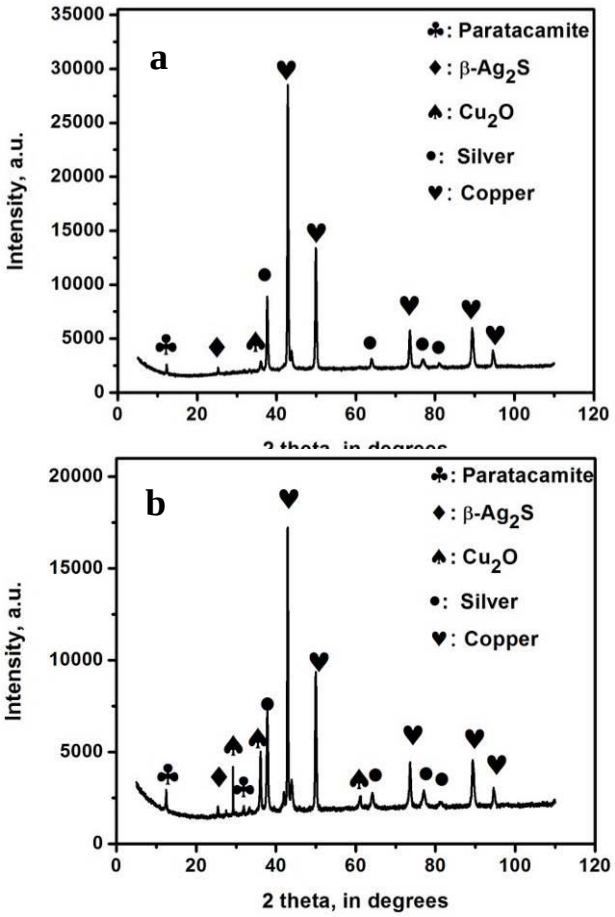


Fig. 4. XRD pattern of different coins (a) coin no 3 & (b) coin no 5 showing the formation of corrosion products of copper and silver.

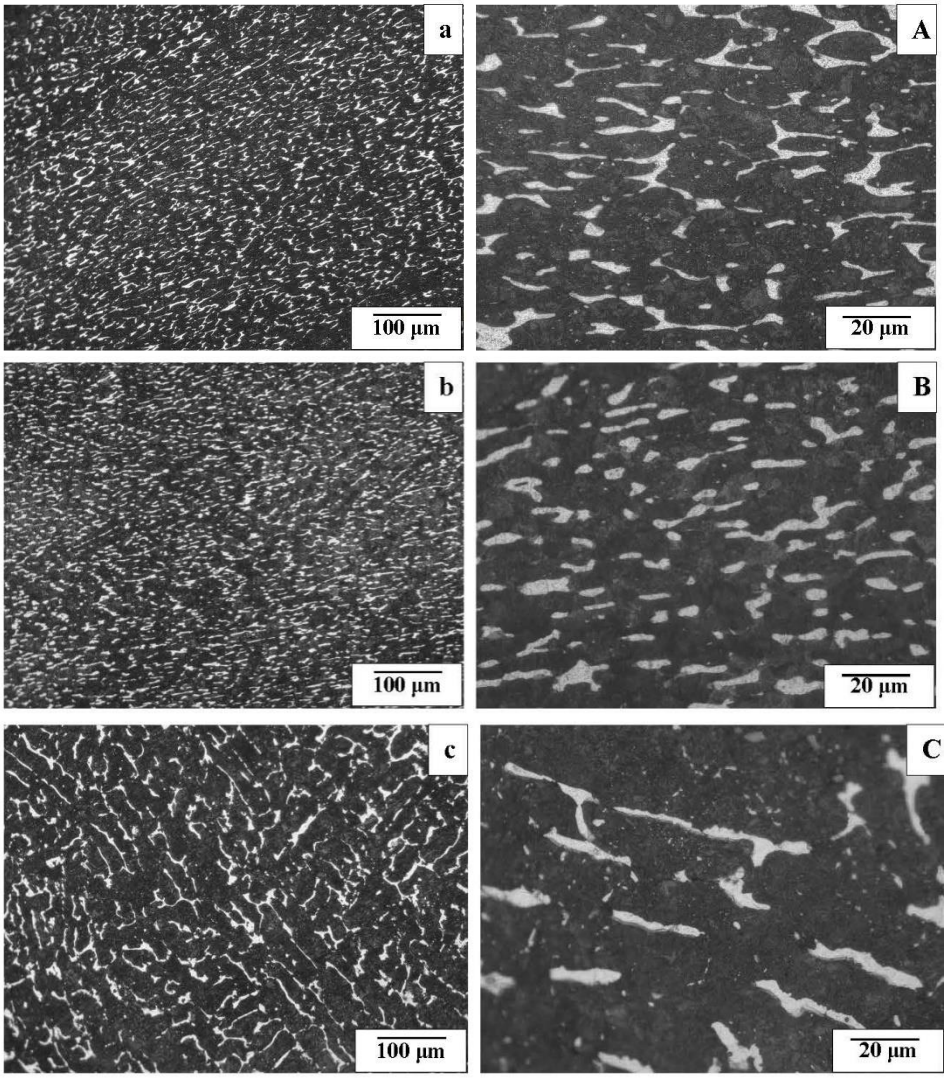
In general, $Cu_2(OH)_3Cl$ is rarely formed in the coins; however, the investigated coins were collected from the river bed, and the coins have been exposed to all the three conditions required for the formation of this compound i.e. chloride, moisture, and oxygen. The presence of chlorine was also observed in the XRF spectrum.

Microscopic Examination

Microstructural Examination

Figure 5 shows the optical micrographs of the coins at different magnifications. The formation of a dendritic structure may be clearly seen. There is a slight difference in the morphology and arrangement of dendrites. Secondary arm in dendrites is visible only in coin no.3 (Fig. 5c); however, in other coins, there is the formation of only primary dendrite. The presence of dendrites in the optical micrograph indicates that the coins might have been produced by casting, and after solidification, they were not subjected to any type of heat treatment. The variation in morphology of the dendrite

may be due to the difference in the cooling rate adopted for solidification. The dendrites forming during solidification have primary, secondary, and even ternary arms. No signature of the deformation and heat treatment was observed in the optical micrographs. Thus, it may be understood that coins were not subjected to any type of deformation and heat treatment. Researchers have not given attention to the microstructural analysis of the copper-silver alloy coins to understand the processing history. Most of the studies have been focused mainly on the silver and silver debased coins. It has been observed that debased silver with different amounts of copper has been a metallurgical tradition to fabricate silver coins during the Sasanian period. Microstructural analysis of the silver-copper coin showed the casted structure with no additional working or minting [10].



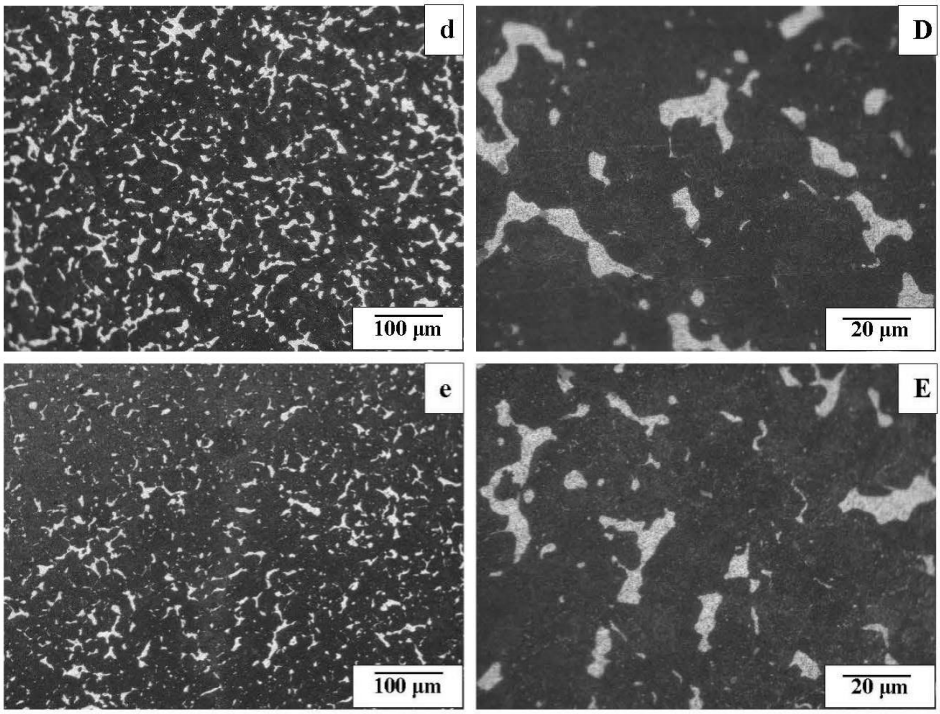


Fig. 5. Optical micrographs at different magnifications showing the dendritic structure (a) coin no 1, (b) coin no 2, (c) coin no 3, (d) coin no 4, & (e) coin no 5.

However, a microstructural study of the sasanian silver coins indicates the evidence of mechanical operations along with annealing treatment as observed in other samples, which may suggest pre-heating of the primary silver before minting [9].

It may be clearly seen from the magnified micrographs (Fig. 5A-E) that the optical microstructure consists of dual-phase, and one phase is black, and the other one is white. The area fraction of the second/white phase was calculated using the Image J software for all the investigated coins and displayed in Table 4. There is no significant difference in the area fraction of the white phase in all coins; however, the area fraction is lowest in coin no 5.

Table 4. Area fraction of the white phase in all the coins.

Coin number	Area fraction of white phase
1	10.68
2	13.70
3	11.05
4	14.34
5	8.33

The elemental composition of both microstructural phases was determined using SEM-EDS. The percentage of silver was found to be higher in the second phase (45 wt. %) in comparison to the dark phase (14 wt.%). These results are in good agreement with the earlier studies [10]. The copper-silver alloy phase diagram is shown in figure 6. It may be seen from the phase diagram that the maximum limit of the solubility of copper in silver at the eutectic temperature (779 °C) is 8.27%, and it decreases with a decrease in temperature [17]. This limited solubility results in a supersaturated solid solution of copper and silver.According to the copper-silver phase diagram, silver-rich structure exists in the supersaturated state in which silver 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 [18].

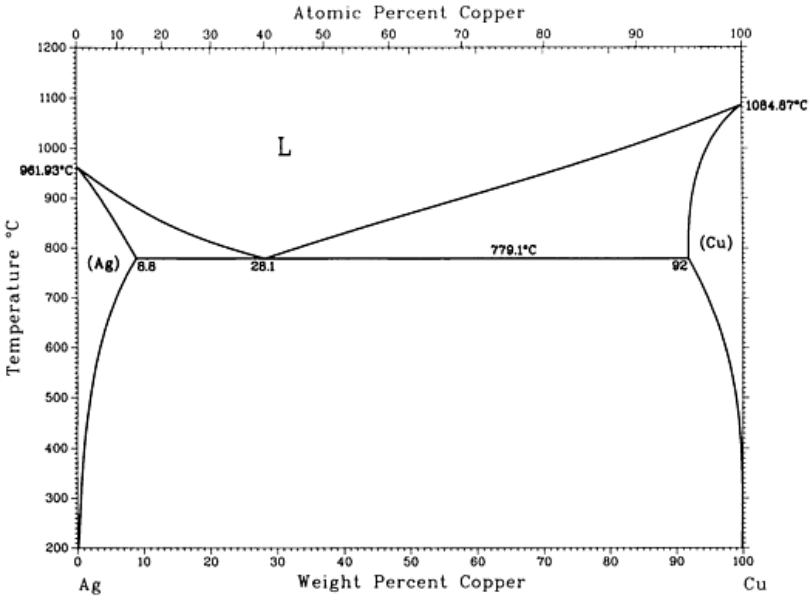


Fig. 6. The copper-silver alloy binary phase diagram [17].

The microstructure of any material can be influenced by various factors, such as manufacturing methods (heat treatment, casting, forging etc.), cooling rate, and material composition [19]. It is very important to mention that the processing history of any ancient metal object can be determined by microstructural analysis. The average value of the microhardness for all the coins is shown in figure 7, and it was found to be in the range from 83 Hv to 95 Hv. The low-copper silver alloy was used to increase the hardness of silver by adding copper to silver in making coins. The addition of copper increases the mechanical strength of the material.

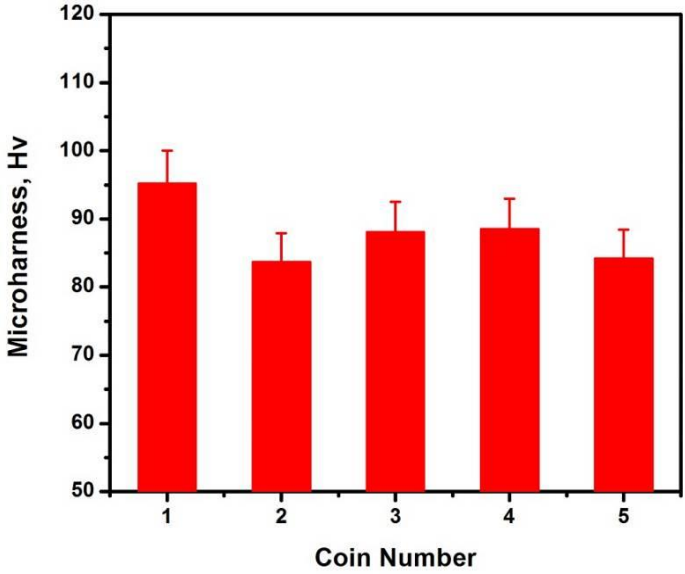


Fig. 7. Microhardness of all investigated copper-silver alloy coins.

Corrosion Behavior

In order to get the morphology and elemental composition of the corrosion product, coins were examined through SEM-EDS. The corrosion layer was found to be adherent and uniform in some coins. The main constituent of the corrosion layers was identified as copper, silver, and oxygen. Based on the electro potential series, the reactivity of the copper is higher than silver towards the oxygen (Fig. 8).

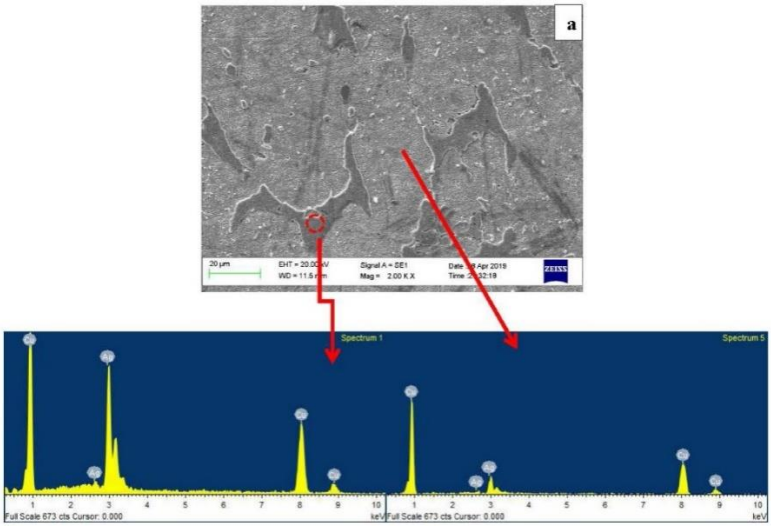


Fig. 8. SEM micrographs of coin no 3 showing the dual-phase microstructure and EDS spectrum for both phases.

Thus, it may be understood that a uniform layer formed on the surface is mainly of cuprite. Morphology of the corrosion products was seen at higher magnification and displayed in figure 9. It is quite obvious from figure 9 that particles are globular in shape, and EDS analysis showed the presence of dominant peaks of copper and oxygen in the spectra, and that confirms the formation of copper oxide. The green pigment formed in the localized region shows the cuboidal shape and presence of characteristic peak of Cu and O along with the chlorine was detected by EDS, and it indicates the formation of paratacamite. The formation of paratacamite was also confirmed from the XRD analysis. The presence of Si may be due to the dust deposited on the surface of the coins.

This degradation process can significantly compromise the conservation status of valuable works of art and modify the object's surface appearance transforming it into a greenish powder. However, stable degradation products can also be formed on the metal substrate, thus creating a passive protective layer, known as "noble" patina. Therefore, it is important to identify the chemical composition of surface patinas since they can strictly affect both surface reactivity and appearance of the metal artifacts, which have to be considered in the identification of the most appropriate conservation materials and methods.

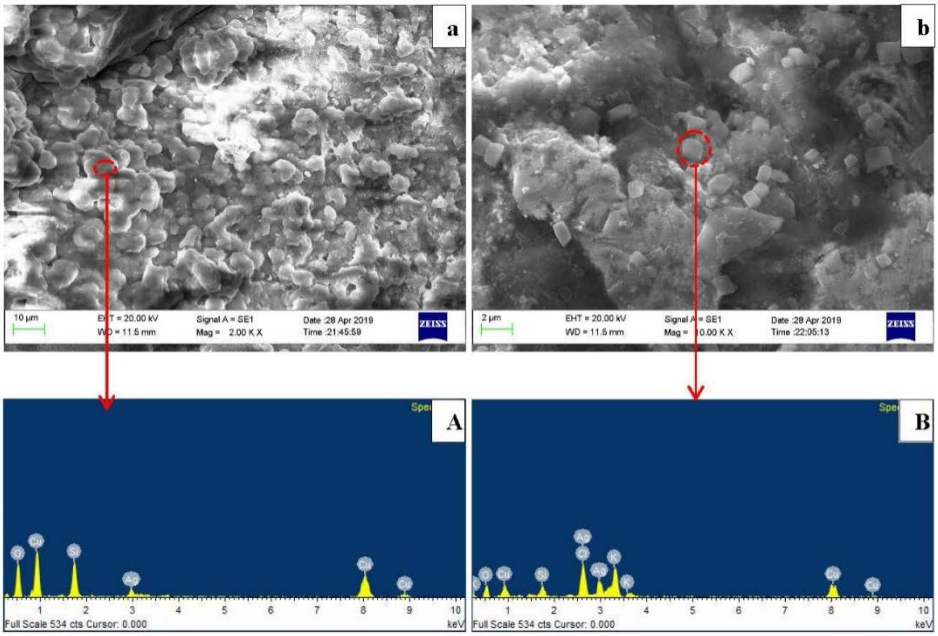


Fig. 9. SEM micrographs and corresponding EDS spectrum of the different types of corrosion products formed on the surface of the coins (a, A) globular Cu_2O in coin no 3 & (b, B) $Cu_2(OH)_3Cl$ in coin no 5.

Conclusions

The Sasanian Empire was one of the most prosperous and dominant state in the ancient world, and different types of metal coins were used in that period, and these coins are known as Sasanian coins. In this investigation, five Indo-Sasanian coins of Gurjara-Pratiharas dynasty were scientifically examined to study the chemical composition and microstructure. Indo-Sasanian coins were derived from the Sasanian coins and probably transmitted to India by the Alchon Huns. Macroscopic examination of the coins showed the crown posed face of the king towards the right on the obverse side.; however, the fire altar flanked by vertical strings of diamond-shaped beads, and deities at each side of the fire altar on the reverse side. These coins are dated to 8th to 9th century on the basis of iconography with the help of archaeologists of the Archaeological survey of India, Lucknow. The XRF results showed that the coins were made of the copper-silver alloy, and iron and lead are present as impurities. The presence of chloride in the localized region indicates that the corrosion is active in nature. The presence of a dendrite structure confirms that coins were manufactured by casting method. Optical microscopy also showed that the coins were not subjected to any type of heat treatment or any type of deformation. Microstructure consists of dual-phase structure darker phase is rich in copper content, and white is rich in the silver. Area fraction of silver-rich phase was found to more or less similar in all the investigated coins. The average value of the microhardness was found to be in the range from 83 to 95 Hv. The presence of paratacamite peak in the XRD spectrum suggests the presence of active corrosion, and conservation treatment is very important to avoid the further deterioration of the coins.

Acknowledgment

The authors are thankful to Shri Ghanshyam Lal, NRLC, Lucknow and archaeologist of the ASI, Lucknow for providing help in conducting XRF experiments and dating of the coins respectively. We are thankful to Mr. Vishal Jain for his help in providing the coins.

References

[1] B. Sodaei, P. MasjediKhak, and M. Khazaie: Natural Sciences in Archaeology, 4 (2013) 211-215.

[2] N. Schiindel, M. Alram, R. Gyselen, and R. Schaff, Sylloge NummorumSasanidarum-The Schaaf Collection, JSTOR, Austrian Academy of Sciences Press, 1st Edition (2014)

[3] A.V. Ham-Meert, F. W. Rademakers, P. Claeys, F. Gurnet, R. Gyselen, B. Overlaet, and Patrick Degryse: Archaeological and Anthropological Sciences, 11 (7) (2019) 3375-3388.

[4] M. Hajivaliei, M.L. Garg, D.K. Handa, K.L. Govil, T. Kakavand, V. Vijayan, K.P. Singh and I.M. Govil: Nuclear. Instruments and Methods in Physics Research Section B, 150 (1999) 645-650.

[5] M. Alram, R. Gyselen, Sylloge NummorumSasanidarum Paris–Berlin–Wien, Band I. Ardashir I.-Shapur I., Verlag der Österreichischen Akademie der Wissenschaften, Vienna, 2003.

[6] N. Schindel, Sylloge NummorumSasanidarum Paris–Berlin–Wien, Band III. Shapur II.-Kawad I./2. Regierung.

[7] K. Uhlir, R. Padilla-Alvarez, A. Migliori, A. G. Karydas, I. BozicevicMihalic, Milko Jaksic, Ivana Zamboni et al.: Microchemical Journal, 125 (2016) 159-169.
[8] B. Sodaei, M. Hajivaliei, and F. KhademiNadooshan: Mediterranean Archaeology & Archaeometry, 13 (1) (2013) 161-170.
[9] M. Mortazavi, N. Sogand, R. Khanjari, and Davoud Agha-Aligol: Archaeological and Anthropological Sciences, 10 (8) (2018) 1831-1840.
[10] O. Oudbashi, A. Hasanpour, A. Jahanpoor, and Z. Rahjoo: STAR: Science & Technology of Archaeological Research, 3(2) (2017) 194-205
[11] H.P. Ray, Negotiating Cultural Identity: Landscapes in Early Medieval South Asian History, Routledge India, 1st Edition, (2019) 161–163.
[12] J.S. Deyell, The Monetary Dimensions of the Vigrahapala and AdivarahaDramma Coinage: an Exploratory Essay, IIRNS Publication, 39 (2015).
[13] P. Craddock: ISIJ international, 54 (5) (2014) 1085-1092.
[14] S.R.B. Cooke, and Stanley Aschenbrenner: Journal of Field Archaeology, 2 (3) (1975) 251-266
[15] T.P. Craddock., and N.D. Meeks: Archaeometry, 29 (2) (1987):187-204.
[16] S.R.B Cooke, and S. Aschenbrenner: Journal of Field Archaeology, 2 (3) (1975) 251-266.
[17] P. Northover, S. Northover, and A. Wilson, Microstructures of ancient and historic silver. In: Metal 2013, 16-20 Sep 2013, Edinburgh, International Council of Museums ICOM-CC, (2013) 253-260.
[18] D. Scott, A. Ancient Metals: Microstructure and Metallurgy: Iron and Steel. Vol. 4. Lulu. com, (2011).
[19] V. Bird, and H. Hodges: Studies in Conservation 13 (4) (1968): 215-223.

Creative Commons License

This work is licensed under a Creative Commons Attribution 4.0 International License.