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A CASE STUDY OF A SET OF COIN SILVER SPOONS FROM MOHAMED ALI MUSEUM, CAIRO, EGYPT

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Abstract

In this research, a set of four coin silver spoons that belong to prince Mohamed Ali and were struck in Egypt in the name of Sultan Abdul Hamid II (1293-1327 AH / 1876-1909 AD) is investigated. The set was exhibited at Prince Mohamed Ali Museum, in Cairo, Egypt. As it has never been studied before, the study aims to identify the manufacturing technique and the deterioration aspects. Visible imaging and geometrical documentation were undertaken to reveal the preservation condition of the objects. A USB Digital microscope was used to examine the coin spoons. Portable x-ray fluorescence (XRF) was used for the elemental analysis of the alloy, while Scanning Electron Microscopy coupled with energy dispersive X-ray (SEM-EDX) was used in order to identify the corrosion products. Metallographic Microscope was used to identify the alloy microstructure to explore the manufacturing technology. Portable x-ray fluorescence (XRF) showed that the coin spoons are made of coin silver, which is an alloy of silver and copper. While the results of scanning electron microscopy coupled with energy dispersive X-ray (SEM-EDX) confirmed the portable x-ray fluorescence analysis that the coin spoons were made of a silver-copper alloy, SEM-EDX analysis also showed the presence of elemental corrosion layers like C, S, and Cl. An investigation with metallography of the crescent-like shape at the end of the hand part of the coin spoon found that the hand area was cast then twisted, It was also revealed that the coin part had been cast first, and then struck afterwards, as seen by the cold-worked dendrites that were deformed.

***Keywords**: Coin spoon, Tughra, Sultan Abdul Hamid II, Silver- copper alloys, tarnishing, microstructure, XRF, SEM-EDX.*

1. Introduction

The use of silver in various products led to the development of a unique metalworking technique that was influenced by the art of all cultures and was commonly used to create a variety of beautiful things [1]. Some examples include coins, silverware, jewelry, and decorative arts [2]. The items under studyare an Ottoman coin spoon made of silver alloy from the nineteenth century. A spoon is a kind of eating utensil that has a small, round or oval bowl (also known as a head) attached to the end of a handle. The coin-shaped spoons were produced between 1890 and 1920 because there was no demand at the time from collectors for these older coins. According to local artisans, coins are the ideal raw material to use when making spoons. So instead of melting them down, they chose to turn them into a saleable commodity. So they pay with coins. A coin that may be used as currency will be used to make the handle, the bowl, or more than one part of a coin spoon. The value of a coin is not correlated with how old it is [3]. Pure silver is alloyed to change its mechanical and physical qualities due to its brittleness. The improved qualities make the alloy appropriate for a number of uses [4, 5]. Cast silver and copper alloys have been used to make both beautiful and useful objects since at least the third

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millennium BC[6]. The Binary Alloy, which is composed of an alloy of silver and copper and named Bullion alloy [7] is one of the most popular silver alloys [8,9] and there is a percentage of impurities from tin, arsenic, lead, and antimony [10]. The corrosion process, which results in a brownish-black tarnish, is responsible for the deterioration of silver–copper alloys. The aesthetic value of the artefact is diminished as a result of this tarnish [11]. Increased intergranular cracking, regions of ductile fracture, and brittle intergranular fracture were the results of the item's having corrosion layers, which are related to long-term pollution and oxidation [12,13]. This type of corrosion occurs around the circumference of the copper grains as a result of direct and deep contact between copper and silver with different electrochemical potentials, which leads to the corrosion of the less noble copper, which becomes anodic and selectively melts in the lower anodic regions [14].
Precious metal artefacts such as silver alloys are characterized by Scanning Electron Microscopy (SEM) and EDS surface analysis as well as optical microscopy [15, 16]. The elemental analysis by XRF is very important to understand the nature and composition of the alloy by taking several spots on the object [17]. Examining the microstructure of an the silver –copper alloys is one of the best ways to figure out how it was made, how it was treated with heat, and what caused it to break. The alloy's microstructure changes at the same time as it is homogenized, heated, annealed, or treated with a solution or a precipitate [18,19]

The four coin spoons consisted of twisted handle ending with a crest and a silver coin struck in Egypt in the name of Sultan Abdul Hamid II(1293-1327 AH / 1876-1909 AD) which is recorded as number 259. They are preserved at Prince Mohamed Ali Museum, Cairo, Egypt. They are categorized as a fine silver teaspoon or coffee spoon or salt spoon. Four pieces of the twenty piasters silver denomination are attributed to this model, three of them (pieces No. 1.3.4), were struck in the tenth year of Sultan Abdul Hamid's reign, i.e. in the year 1302 AH / 1884 AD. While the piece No. 2 was struck in the eleventh year of the Sultan's reign, that is, in the year 1303 AH / 1885 AD**.** they were 9cm high, 17g weight.

2- Materials and Methods

Documentation of the studied object

Visible imaging was performed with Nikon Digital camera D3200, and fitted with a Nikon Nikkor 18-55, which was used in documentation, to detect clear photos of the four coin spoons, while geometric documentation by AutoCAD 2D 2020 and Adobe Illustrator2020 were performed to formulate the deterioration map, to reveal the details and the deterioration aspects of the objects.

USB Digital microscope:

A handheld USB digital microscope (model PZ01; manufactured by Shenzhen supereyes co. Ltd, China) with the following technical specifications was used to examine the coin spoons. The camera has an image sensor with 0.3 mega pixels, a magnification factor that ranges from 10 to 500 times, photo capture resolutions of 640 x 480 and 320 x 240, and an LED illumination light resource that can be adjusted via a control wheel.

Sampling

There is no doubt that the samples taken from the coin spoons were very small . Two representative samples were carefully taken from the tip of a coin spoon as shown table 1.

Portable XRF:

A portable X-ray fluorescence analyzer (XRF): NITON/XLt 8138 (USA), with software version 4.2E for 1 minute. This type of analysis was used to analyze the elemental composition of the coin spoon.

Scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDX)

Scanning electron microscope (Model Quanta 250 FEG (Field Emission Gun)—FEI Company, Netherlands, attached with an EDX Unit (Energy Dispersive X-ray Analyses), with an accelerating voltage of 30 K.V., magnification of 14x up to 1000000, and resolutions for Gun.1n), was used to examine the tarnishing layer of the coin spoons without sputtering with gold. This was performed at the Egyptian Mineral Resources Authority's central laboratory division in Giza, Egypt.

Metallographic Microscope:

Microstructural examination was carried out using a metallographic microscope to figure out how the set was made. The sample taken from the edge of one of the coin spoons, was examined using a metallographic microscope (Olymus Optical Microscope BX41M) with a magnification of 1100$_X$

to 5500x. The etching process was by means of the etching solution consisted of acidified potassium dichromate which composed of 10 ml sulfuric acid H_2S0_4, 100 ml potassium dichromate saturated K_2Cr_{207} in water, 2 ml sodium chloride, saturated NCI solution[20] .

3. Results:

3.1. Visual Examination

3.1.1 Investigation of the four coin spoons revealed that they consist of two parts which are the coin and the handle which are welded together. All the coin spoons were covered with different corrosion products ranging in the color from a brownish to black layer, fingerprint marks, some pitting, and the presence of adhesive residues and sticky labels which were used in the numbering process in the Museum. There is a missing part in the crescent of coin spoon number two and a slight warp in its twisted handle.
3.2.2 The coin spoons were made by welding the cast coin to the twisted handle which ended with a crescent shape as shown Fig. [1].

3.2 Examinations by USB microscope:

By using USB microscope, it revealed that the bowel coin of the spoon is distinguished by the fact that the writings and decorations of the face came from the tughra of Sultan Abdul Hamid II, which reads from bottom to top "Abdul Hamid Khan bin Abdul Majid Muzaffar", and to the right of the tughra in the empty space is a plant branch, and below the tughra is the value of cash, which is the letter "sh", above it is the number indicating the value of the coin, and below it are two quiveres for arrows, from which two laurel branches rise and form a circular decorative frame complete with a drawing of seven stars. As for the inscriptions and decorations on the back, they consist of two parallel lines that read: "Darb fi Masr" written in Thuluth script. In typical writing conditions, many consider the Thuluth script style to be the most difficult and hardest of all Arabic scripts. Thuluth calligraphy grows increasingly difficult. Developed in the ninth century A.D., the Arabic Thuluth alphabet and calligraphy are widely used today [21].

The return yaa in the preposition "fi" is a separator between the two lines, and the bottom of the two lines is the date of the Sultan’s assumption of power, which is 1293 AH, and the number indicating the year of minting the cash is higher than the letter "baa." The inscriptions on the back are surrounded by two vegetal branches, which are two laureate branches connected from the bottom of the coin and wrapped around the edges of the coin, separated by three five-pointed stars from the top as shown in Fig [2]. The geometric documentation of the four coin spoons illustrating the deterioration aspects as shown in Fig [3].

3.3. Portable XRF:

The elemental analysis of the alloy of the coin spoons was used by Portable XRF to identify the proportions of the constituent elements of the alloy by analyzing some points as shown in tables [2] and [3]. However, before beginning the analysis, care must be taken to thoroughly clean the surface of the analysis point, especially of any corrosive substances.

3.4. Scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDX)

The sample has been subjected to Scanning Electron Microscopy combined with Energy Dispersive X-ray Spectrometry (SEM-EDS) in order to determine the chemical composition of the alloys. The findings showed that all samples were made of silver-copper alloys and that various layers of elemental corrosion, including those containing C, S and Cl had been found as Fig. [4] Shows the surface of the silver-copper alloy with the presence of sulphur , carbon and chloride.

3.5. Metallographic Microscope:

The results of the metallographic examination of the sample taken from the hand area showed that the technique of its manufacture was by the casting technique, and this appears through the dendritic shape as shown in Fig. [5a and 5b]. The results of the metallographic examination of the sample taken from the coin area showed that the technique of its manufacture was by the casting technique then the coin was minted as it appears through the cold – worked distorted dendrites shape as shown in Fig.[5c and 5d].

Discussion:

The elemental analysis by XRF was carried out for several points of the coin and twisted handle which showed that the metal that makes up the coin spoons is an alloy of silver and copper known as coin silver. It was called "coin silver" because a lot of it was made by melting down silver coins. As the most common definition of coin silver means that the item contains 90% silver and 10% copper by mass [22]. The elemental analysis by XRF revealed that the composition of the coin is 91% silver and 7.3% copper as well as trace amounts of the elements Antimony(Sb), Tin(Sn), Indium(In), Lead(Pb), Coblat (Co), Zinc (Zn), Iron(Fe), Manganese (Mn), Chromium (Cr), Vanadium (V), Titanium (Ti). While the composition of the handle was 88.48% silver and 7.95% copper as well as trace amounts of the elements Sb, Sn, In, Pb, Co, Zn, Fe, Mn, Cr,V,Ti as shown in Table[2, 3]. The metallic elements that are added to copper to make alloys alter its corrosion behaviour. The more noble (Ag) hastens corrosion, whilst the most active (Sn, Zn, Pb) supports cathodic protection for a limited time dependent on environmental aggressiveness [23].

Due to the interaction of silver alloys with atmospheric pollution gases, silver oxide is produced when silver absorbs oxygen molecules, which are then converted into oxygen ions (O_2). Generally, silver oxide (Ag_2O) is created when metal cations and oxygen ions combine. This oxide layer is a protective layer. When humidity levels are high, electrochemical processes take place [24-26]. Also, because they are there, silver carbonates can form as a result of corrosion, especially when O_3 and UV light are present [27]. Despite silver's durability, it can react with oxygen, sulphur compounds (H_2S or COS), and humidity in the air, leading to a brownish-black tarnish on an object's surface [28], which results in the formation of a black tarnish layer on the surface of the silver, It is evident from the elemental analysis by SEM-EDX of the surface of the silver-copper alloy that sulphur and carbon are present. It is regarded as one of the most hazardous gases for silver since it makes the alloy lose its shine and exposes it to corrosion by forming a dark film that eventually turns black, a phenomenon known as silver tarnishing. Therefore, the presence of acanthite (Ag_2S) may be assumed to be caused by sulphur pollutants, which play an important role in the presence of the black corrosion products [27, 29]. Also present in the indoor atmosphere are gases such as O_2, O_3, H_2O_2, and H_2S, as well as carbonyl sulphide (COS), which was discovered to be the controlling sulfur-bearing compound [30]. It is also evident from the elemental analysis by SEM-EDX of the surface of the silver-copper alloy that chloride is present, as in addition to producing a surface deposit that might be visually off-putting, fingerprints can also cause the metal to corrode and eventually lose its original surface [24, 27].

Metallography investigation of the crescent shape at the end of the coin spoon's hand part revealed that the hand area was cast then twisted, as twisting is a type of cold working. The dendritic shape of this portion demonstrates this. The technique of modifying the shape of a metal's microstructure below the temperature at which it would re-crystallize is known as cold working. Cold working shapes the metal by using procedures such as hammering, turning, elevating, drawing, and so on [13], but it also strengthens it (or strain-hardened). The strengthening is caused by the increasing number of dislocations. When the stress becomes too great, the joints begin to slip. As the applied stress increases, the deformation causes the grains to appear deformed [31, 32]. A metallographic examination of the coin part indicated that it was first cast and subsequently struck, as seen by the cold-worked, distorted dendrites. Several sorts of flaws may occur in casting as a result of unsuitable or unsatisfactory raw materials used in moulding; or the application of unsatisfactory moulding or casting practise by the manufacturer [33, 34]. As well as when the grains are hammered, their shape changes because of slip, dislocation movement, and the fact that dislocations form as a result of working [13, 35].

Table. 1. Illustrates the Examination and analysis of samples

No.	Type of Sample	Examination	Analysis
1	The coin spoon number 1, 2		XRF
2	Thin sample of the edge	SEM	SEM-EDX
3	Thin sample of the edge	Metallographic Microscope	
4	The four coin spoons	Examinations by USB microscope	

Table 2. Shows the weighted ratios of the coin elements

The coin	Ti	v	Cr	Mn	Fe	Zn	Co	Pb	In	Au	Sn	Sb	Cu	Ag
Spot 1	0.01 ± 0.58	**0.01 ± 0.30**	**0.01 ± 0.18**	**0.07 ± 0.13**	**0.09 ± 0.11**	**0.18 ± 0.05**	**0.03 ± 0.06**	**0.12 ± 0.02**	**0.03 ± 0.16**	**0.04 ± 0.04**	**0.58 ± 0.59**	**0.59 ± 0.75**	**6.78 ± 0.22**	**91.4 ± 1.19**
Spot 2	0.40 ± 0.88	**0.01 ± 0.42**	**0.07 ± 0.27**	**0.01 ± 0.15**	**0. 1 ± 0.14**	**0.06 ± 0.05**	**0.1 ± 0.06**	**0.17 ± 0.03**	**0.14 ± 0.20**	**0.01 ± 0.04**	**0.38 ± 0.69**	**0.49 ± 0.95**	**8.0 ± 0.28**	**90.7 ± 1.57**
Av.	0.20	**0.01**	**0.04**	**0.04**	**0.09**	**0.1**	**0.06**	**0.14**	**0.08**	**0.02**	**0.61**	**0.54**	**7.39**	**91.0**
Sd.	0.27	**0**	**0.042**	**0.042**	**0.007**	**0.084**	**0.049**	**0.035**	**0.077**	**0.021**	**0.33**	**0.07**	**0.86**	**0.48**

Note: nd= not detected Av= Average Sd= Standard deviation

Table 3. Shows the weighted ratios of the hand elements

The handle	Ti	v	Cr	Mn	Fe	Zn	Co	Pb	Cd	Pd	Ni	In	Au	Sn	Sb	Cu	Ag
Spot 1	0.03 ± 1.01	0.39 ± 0.70	0.02 ± 0.30	0.02 ± 0.20	0.40 ± 0.25	0.10 ± 0.08	0.02 ± 0.11	0.24 ± 0.05	0.03 ± 0.07	0.03 ± 0.07	0.02 ± 0.12	0.10 ± 0.30	0.19 ± 0.09	1.66 ± 1.00	0.70 ± 1.42	8.24 ± 0.40	87.79 ± 2.16
Spot 2	0.17 ± 0.51	0.32 ± 0.99	0.07 ± 0.46	0.40 ± 0.25	0.04 ± 0.14	0.05 ± 0.23	0.96 ± 0.19	0.02 ± 0.68	0.12 ± 0. 23	0.03 ± 0.07	0.14 ± 0.28	0.02 ± 0.83	0.19 ± 0.09	0.23 ± 0.22	0.03 ± 3.99	7.66 ± 0.78	89.17 ± 1.49
Av.	0.0.3	0.35	0.04	0.2	0.2	0.07	0.4	0.13	0.07	0.03	0.08	0.05	0.19	0.94	0.36	7.95	88.48
Sd.	0.09	0.04	0.03	0.2	0.2	0.03	0.6	0.15	0.06	0	0.08	0.06	0	0.99	0.47	0.41	0.97

Fig. [1]. show the observe and the reverse of the four coin spoons, Fig.1a represents the observe, and the Fig.1b represents the reverse.

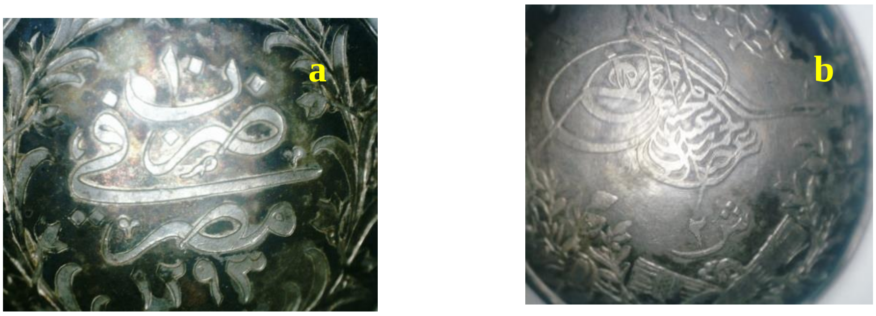


Fig. [2] Shows the USB images of the coin's deterioration aspects : the front of the coin (a) and the tughra Sultan Abdul Hamid II on the reverse (b).

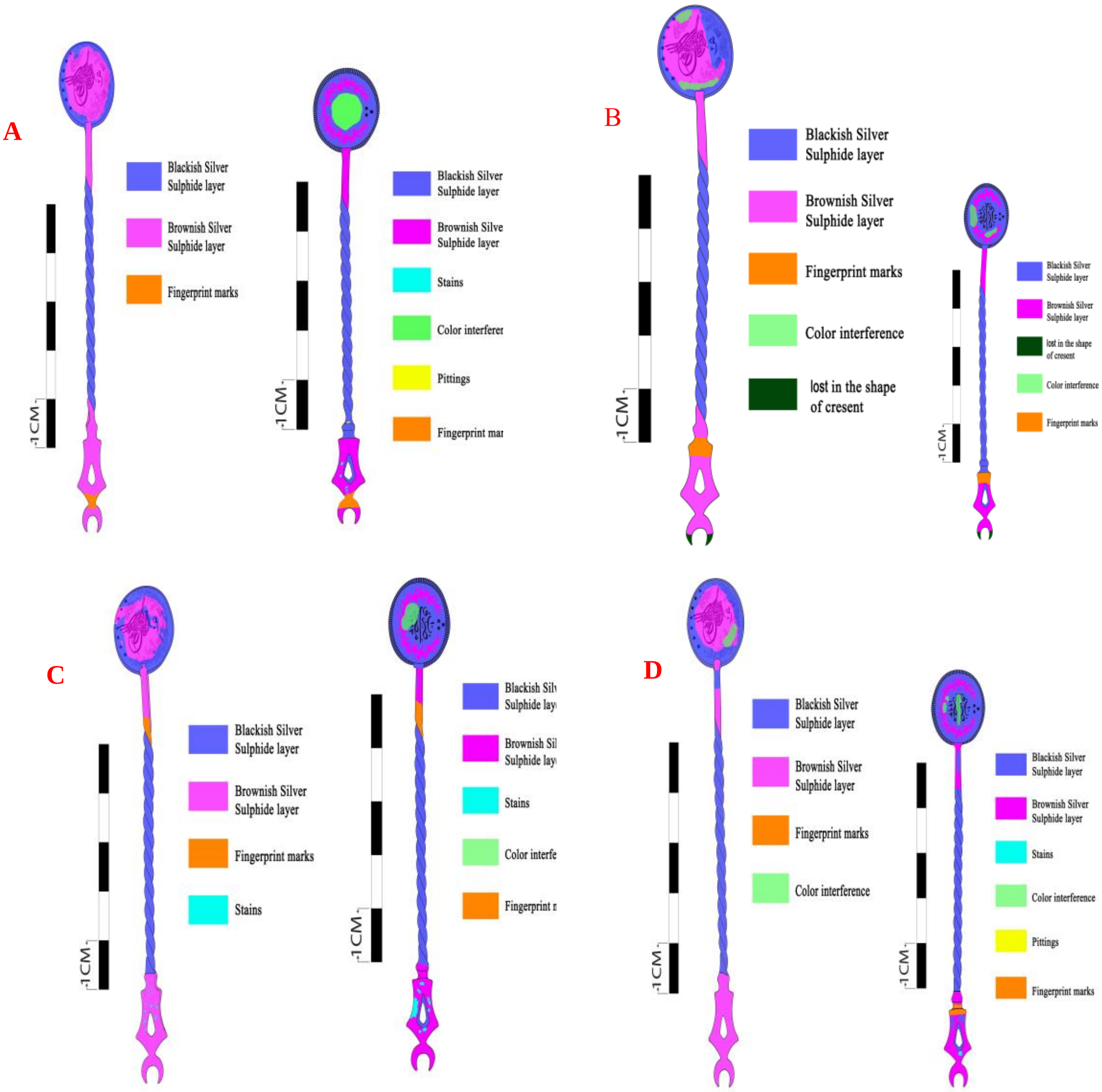
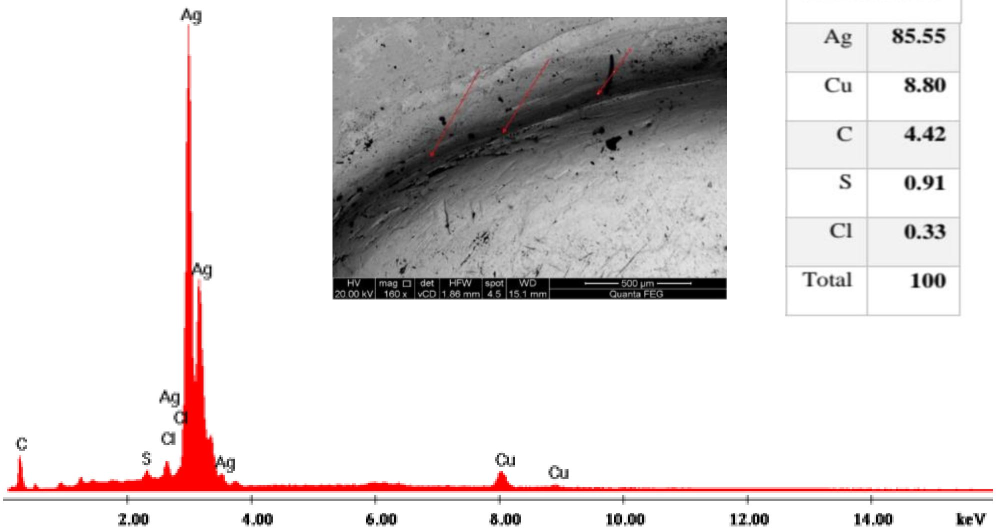


Fig. [3]. Show deterioration aspects of the obverse and the reverse of every spoon as Fig.3A represent the spoon NO.1, Fig.3B represent the spoon NO.2, Fig.3C represent the spoon NO.3, Fig.3D represent the spoon NO



Element	wt%
Ag	85.55
Cu	8.80
C	4.42
S	0.91
Cl	0.33
Total	100

Fig. [4]. shows blowholes on the surface of a silver-copper alloy with corrosion elements present.

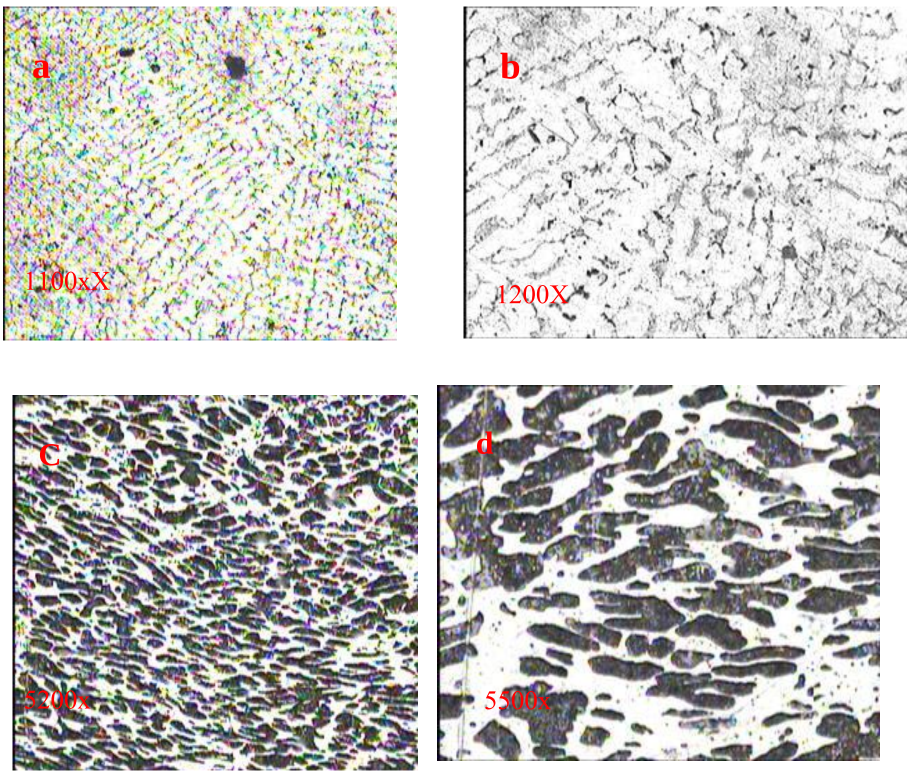


Fig. [5] Show the microstructure of the coin spoon as fig. [5 and 5b] represents the hand of the spoon while fig. [5c and 5d] represents of the coin part.

Conclusions

The investigation demonstrated that there are various deterioration factors resulting from environmental degradation that affect on silver coin spoons. In order to illustrate and have a thorough grasp of the coin spoons' components and rates of degradation, visual inspection, documentation, and analysis were used. The presence of a blackish silver sulphide layer is a sign of silver tarnishing. When there is electrolyte on the metal surface, the air's relative humidity and contaminants have a significant impact. Silver doesn't react with oxygen in normal, dry air. Adsorbed water layers in oxide structures allow corrosive ions to penetrate. Chlorides and sulphide ions enlarge crystallographic flaws in silver oxide, causing local cell corrosion. Silver sulphide conducts electricity better than silver oxide, so corrosion thickens with time.

The gases present in indoor atmospheric corrosion are represented by the oxidants O_2, O_3, H_2O_2, H_2S, and carbonyl sulphide (COS). The composition of the alloy and the its manufacture technique also play a big role in the mechanism of deterioration. Finally, choosing the optimal treatment and conservation techniques is aided by the outcomes attained. The steps of conservation for these sets, which involved entirely eliminating the corrosion layers covering them while maintaining their integrity, will be covered in the second section of this research. So according to the results from the examination and analysis methods that were used to investigate the set of coin spoons , it can be concluded that silver-copper alloys failed due to corrosion, which resulted in brownish-black tarnish. This tarnish alters the object's appearance. The object's corrosion layers denoted long-term pollution and oxidation. Long-term contamination and oxidation led to increased intergranular cracking, ductile fracture zones, and brittle intergranular fracture, which were the causes of the object's corrosion layers. These results will help choose the best method to clean the surface of the set and then apply a suitable protective layer.

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Conflicts of interest

We hereby declare that we have no pecuniary or other personal interest, direct or indirect, in any matter that raises or may raise a conflict with our duties. We also acknowledge that we shall make another declaration to state any change in any matter contained in this declaration within one month after the change occurs and shall provide further information on the particulars contained in this declaration.

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