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Electrochemical Cleaning of Artificially Tarnished Silver

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The tarnishing of silver artefacts surface, that are exposed in museums or kept in storage, is a reason that makes them inappropriate for displaying. In this work the conditions for tarnish removal (horn silver and silver sulphide) from silver artefacts surfaces by an electrochemical galvanic cell of silver/aluminium in sodium carbonate electrolyte are investigated. For this purpose sterling silver drawn sheet coupons were tarnished by different chemical methods so as to produce a corrosion layer containing mainly silver chloride or silver sulphide compounds. An extensive study of the produced corrosion layers was performed by X–ray diffractometry, scanning electron microscopy and surface analysis. Measurements of galvanic current were taken by shorting the corroded silver and aluminium sheet together through a potentiostat. Possible cathodic reactions and their effect on the overall galvanic current are discussed.

Keywords: Sterling silver, tarnish removal, electrochemical cleaning

1. INTRODUCTION

Silver is a noble metal highly appreciated from ancient times until now days. Its physical and chemical characteristics combined with the beauty of its surface appearance, make it an ideal material for producing decorative objects. Silver was used in two principal forms: as the so called “solid” silver objects and as a coating. Solid silver articles consist of alloys with other metals, partly to make the alloy harder, and also to reduce on the amount of silver used [1]. These objects, often containing copper as a major alloying element and lead and gold as impurities, can either be cast directly or cold–worked into the final form. In general, the most commonly employed alloys used to produce objects are: the so called “sterling silver” (92.5% Ag, 7.5% Cu), “coin silver” (90% Ag, 10% Cu), and eutectic or brazing alloy (71.9% Ag, 28.1% Cu). Since most “silver” objects are made from silver–copper alloys, it is important to know the structural characteristics of this type of alloy. The structure of a material not only defines its properties, but can also explain the way it deteriorates.

Tarnishing of silver (formation of a blackish silver sulphide layer) or silver plated collections is a general corrosion process. The presence of electrolyte on the metal surface depends on the relative humidity of the air and the pollutants in the atmosphere. Gases that may be involved in indoor atmospheric corrosion can be O_2, O_3, H_2O_2, H_2S, carbonyl sulphide (COS), (COS is found to be the predominant sulphur–bearing compound), SO_2, HCl, Cl_2, NH_3, NO_2, HNO_3, CO_2, HCHO, HCOOH and CH_3COOH. Furthermore the chemical composition of the alloys, the manufacture and the surface of artefacts play a role in the corrosion mechanism. The different steps of the artefacts restoration have also an influence on their future conservation.

Moisture is a serious environmental hazard; as matter of fact in the presence of atmospheric humidity iron rusts, silver tarnishes faster, and copper and its alloys, brass and bronze, corrode. Condensed water vapor, participates, together with the oxygen molecules, in the capture of electrons from the metal [2]. In high humid conditions, more than two layers of adsorbed water act as bulk water and an electrochemical reaction in bulk solution is expected [3]. However, the low corrosion rate in low humid conditions is attributed to less than a monolayer of adsorbed water, which has more difficulty in conducting protons as described in the Zn–H_2S system [4]. Adsorbed water layers promote the penetration of corrosive substances by introducing irregularities into the oxide structure. Chloride and sulphide ions, likewise, tend to enlarge crystalline defects. Chloride ions easily permeate oxide films leading to corrosion by means of local cells. Sulphide ions, by formation of silver sulphide, gravely distort the crystal structure of silver oxide. Silver sulphide is a better electrical conductor than silver oxide and its cations diffuse with ease through the corrosion film, which, under these conditions, grows following a parabolic law.

In most cases, the principal component of the tarnish film has been identified as acanthite (alpha Ag_2S) [5]. The associated chemical species in the atmosphere are reduced sulfur gases, such as H_2S, and organic sulfur compounds, such as COS [6–11] and dimethyldisulfide (Me_2S_2) [8]. Sources of these species are oil refineries, paper treatment plants, kitchens, rubber, paints, etc. In several cases chlorargyrite (AgCl) has also been identified as a major component [12]. Its origin could be explained by the deposition of chloride–containing airborne particles from combustion processes, dispersion of marine salts or even from the purification treatment of water in urban areas [13].

Removal of tarnishing generally involves the use of an abrasive polish which means removing the silver itself. Another option is different chemical treatments which should be used with a great care because the surface could be over–cleaned and eventually pitted. Electrochemical and electrolytic reduction cleaning are the most common techniques applied to prevent, stabilize and even reverse the oxidation of the metal. The aim of this work is to get a closer insight into the conditions of tarnish removal (horn silver and silver sulphide) from silver artefacts surfaces by an electrochemical galvanic cell of silver/aluminium in an electrolyte of sodium carbonate.

2. EXPERIMENTAL

Sterling silver drawn sheet coupons with dimensions of 2 cm x 5 cm x 0.04 cm, were artificially tarnished by different chemical methods so as to produce a corrosion layer similar to the one formed on metal artefacts either by saline environment, containing mainly silver chloride, or in an urban environment, containing sulphide silver compounds.

AgCl tarnish procedure: Silver coupons were immersed in hot aqueous solution of 0.1 M $CuCl_2$ (50–60 ^oC) for 2, 10, 30 and 60 min The corrosion–patination layer developed gradually and the colour changed from yellowish to brownish–purple. The samples were removed, washed in warm water and allowed to dry in air. An even corrosion layer was produced.

Ag_2S tarnish procedure: The samples were immersed in hot (50–60 ^oC) $Na_2S{\cdot}xH_2O$ 2.5 g/l solution for 2, 10, 30 and 60 min, producing a slightly uneven yellowish to iridescent blue–black corrosion layer. Differentiated areas of the almost clean metal, and areas rich in silver or copper corrosion products, are observed on the samples' surface.

As–tarnished coupons were cleaned using silver/aluminium galvanic cells with cathodic to anodic surface ratio 1/10 in 5wt.% sodium carbonate electrolyte [14]. Galvanic current measurements were taken by shorting the corroded silver and aluminium sheet together through a potentiostat. The surface morphology and chemical composition of the corrosion products developed on the silver coupons before and after galvanic cleaning were studied by means of scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS). Both SEM and EDS characterizations were carried out by using a Quanta 200 FEI scanning electron microscope equipped with a tungsten filament and solid state backscattered electron detector. X–ray diffraction (XRD) patterns were recorded by SIEMENS X–ray Diffractometer 5000 with Cu Kα X–ray source.

3. RESULTS AND DISCUSSION

3.1 AgCl tarnishing and galvanic cleaning

General corrosion in high–silver–content alloys results in the slow conversion of the metal surface to silver chloride [15–17], which forms a brittle finely granular layer. Unfavorable conditions may result in an object being completely converted to silver chloride [15, 16].

To simulate the corrosion patina of aged artefacts, silver coupons were artificially pre–aged by being immersed in hot $CuCl_2$ solution. In this case silver undergoes attack by copper (II) ions in the presence of chloride ions and dissolves according to reaction (1):

$$Cu^{2+}_{(aq)} + 2Cl^{-}_{(aq)} + Ag_{(s)} \leftrightarrow AgCl_{(s)} + CuCl_{(s)} \qquad (1)$$

Several factors render this reaction extremely corrosive, since silver chloride, although insoluble in water does not develop on silver as a protective passivating coating. XRD analysis (Fig. 1) of AgCl aged silver coupons reveals that after 2 and 10 min of immersion both chloroargyrite and nantokite are created on the sample surface while after prolonged immersion only chloroargyrite is detected. It seems that deposited nantokite gradually loses its adherence and precipitates from the metal surface into the solution.

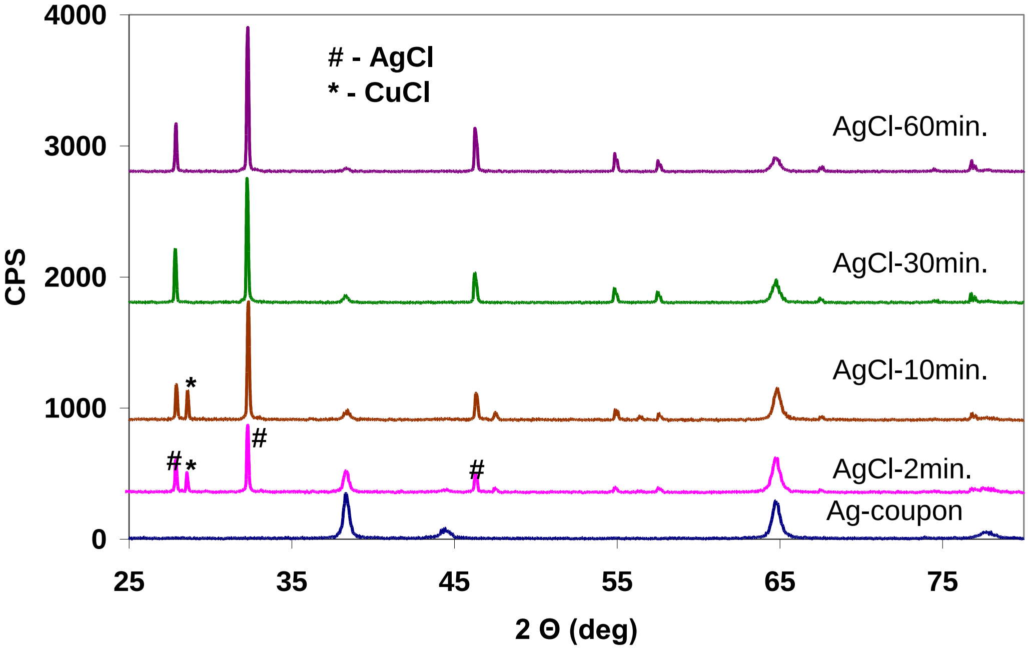


Figure 1. XRD diffractograms of the AgCl aged silver coupons

Table 1 presents some secondary electron (SE) and back–scattered (BS) electron images of pre–aged silver coupons. Their EDS map analysis is presented in Table 2. The BS electron signal is proportional to the atomic number of the sample and is used to create images reflecting the composition of the object under investigation that complement the SE images. The silver rich white areas observed on the BS image after 2 min of immersion could be attributed to alloy surface that has not been corroded yet, while EDS analysis of the dark–grey area reveals the presence of Ag, Cu and Cl proving the formation of a mixture of chloroargyrite and nantokite. After 30 min of immersion SE and BS images confirms a creation of uniform AgCl layer on the alloy surface. EDS analysis apart from Ag and Cl discloses the presence of small quantities of O (~3wt.%) and Cu (~1.5wt.%) so the occurrence of silver oxide or nantokite coming from copper rich δ phase on the alloy surface can not be excluded.

Table 1. SEM images of the AgCl tarnished silver coupons for 2 and 30 min.

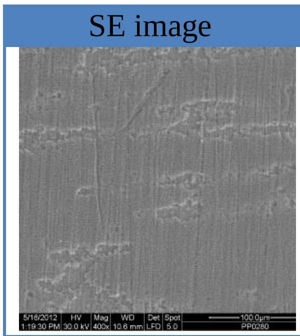
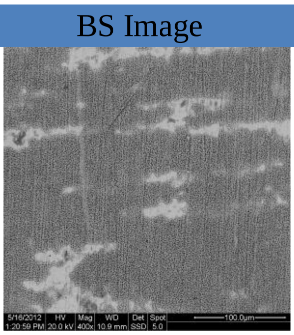
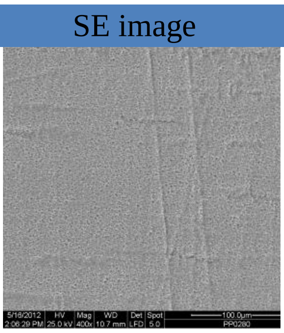
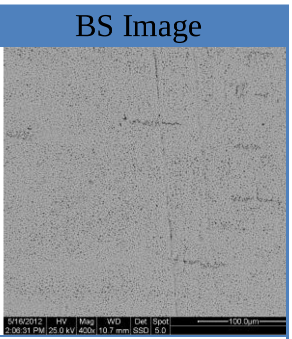
SE image	BS Image	SE image	BS Image
			
AgCl–2 min		AgCl–30 min	

Table 2. EDS map analysis of the AgCl tarnished silver coupons for 2 and 30 min.

	Ag (wt.%)	Cu (wt.%)	O (wt.%)	Cl (wt.%)
AgCl–2 min	76.9	8.7	-	14.4
AgCl–30 min	77.7	1.5	3.0	17.8

As pre–aged silver coupons were galvanically connected to an aluminum electrode in 5wt.% Na_2CO_3 solution and the galvanic current was measured over one hour (Fig. 2). Long term current densities of the order of 5–10 mA/cm^2 were observed for all samples. Also, for coupons aged for 2 and 10 min short time current transients of approximately 45 mA/cm^2 were noticed while coupons aged for 30 and 60 min exhibit transients of 30 mA/cm^2, which last a little longer (up to 130 s). The appearance of the transient current is consistent with AgCl and CuCl reduction, which is governed by large thermodynamic driving force (reactions 2 and 3). This results in the rapid depletion of these layers and apparent silver cleaning.

$$AgCl_{(s)} + e^- \leftrightarrow Ag_{(s)} + Cl^- \qquad E^\theta = +0.22\ V \qquad (2)$$
$$CuCl_{(s)} + e^- \leftrightarrow Cu_{(s)} + Cl^- \qquad E^\theta = +0.14\ V \qquad (3)$$

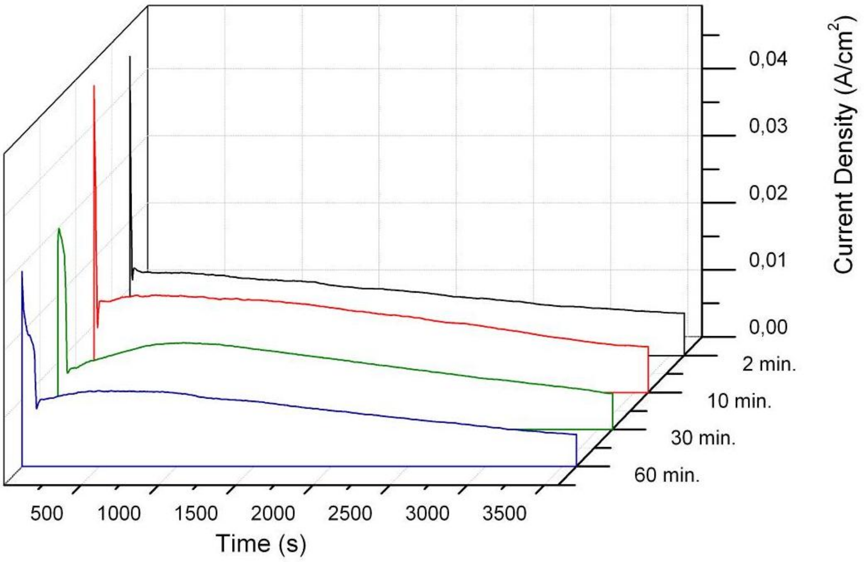


Figure 2. Galvanic current between AgCl tarnished silver coupons for 2–60 min and aluminum anode in 5wt.% Na_2CO_3 solution

Long term galvanic current is governed by hydrogen reduction kinetics according to reaction (4):

$$2H_2O + 2e^- \leftrightarrow H_2 + 2OH^- \qquad (4)$$

The nascent hydrogen may also act as a reducing agent as it evolves from the metal surface. The chlorides are removed and reduced metal is left.

Several SEM images of the cleaned silver coupons after aging for 2 and 30 min are presented in Table 3. On the silver surface aged for 2 min, after cleaning, two different areas can be observed: copper–rich upper part and silver–rich lower part (Table 4). This is also verified by difference in color, the upper part being much darker than the lower part. It seems that during the reduction of a mixture of chloroargyrite and nantokite, copper migrates close to the three–phase border: metal–electrolyte–atmosphere. After cleaning the samples aged for 30 and 60 min, where only AgCl was detected on the surface, a matt gray, porous silver layer has been created, which can be easily scratched from the surface. The chloride presence has not been identified.

Table 3. SEM images of the AgCl tarnished silver coupons for 2 and 30 min after galvanic cleaning treatment

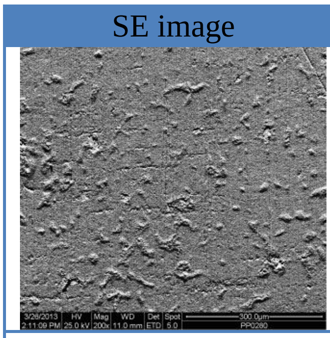
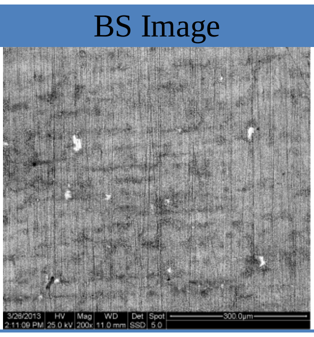
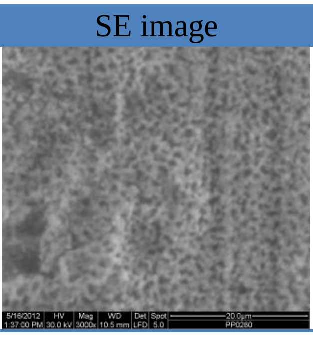
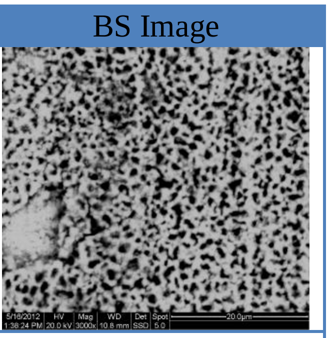
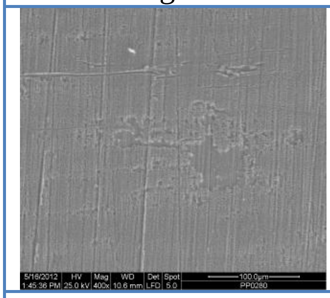
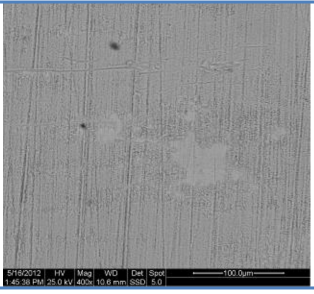
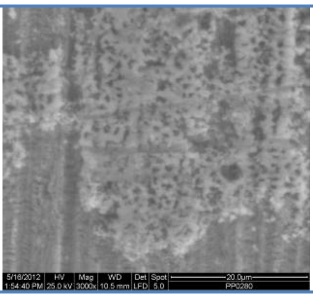
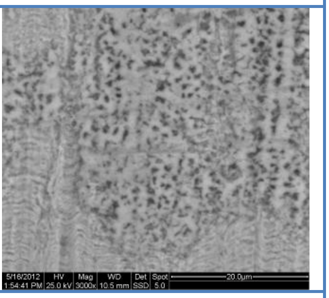
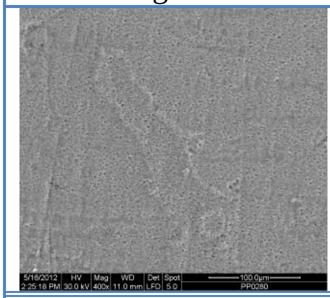
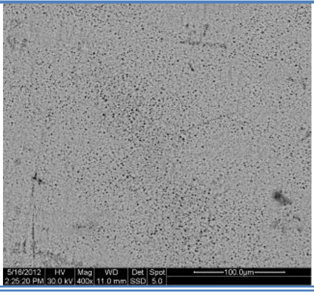
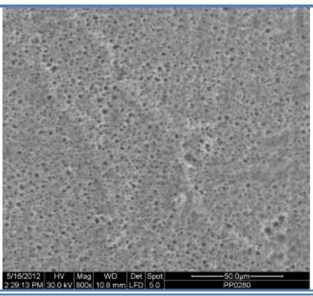
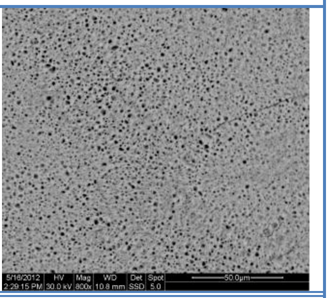
SE image	BS Image	SE image	BS Image
			
AgCl–2min Cleaned–upper part		Detail	
			
AgCl–2min Cleaned –down–part		Detail	
			
AgCl–30 min Cleaned		Detail	

Table 4. EDS map analysis of the AgCl tarnished silver coupons for 2 and 30 min after galvanic cleaning treatment

	Ag (wt.%)	Cu (wt.%)	O (wt.%)	Cl (wt.%)
AgCl–2 min (upper part)	74.7	19.7	5.6	-
AgCl–2 min (down part)	85.9	9.9	4.2	-
AgCl–30 min	100.0	-	-	-

XRD measurements (Fig. 3), also, confirm the absence of chlorides on the sample surface after galvanic cleaning treatment, as well as the total reduction of the corrosion products to the corresponding metals i.e. CuCl to Cu and AgCl to Ag.

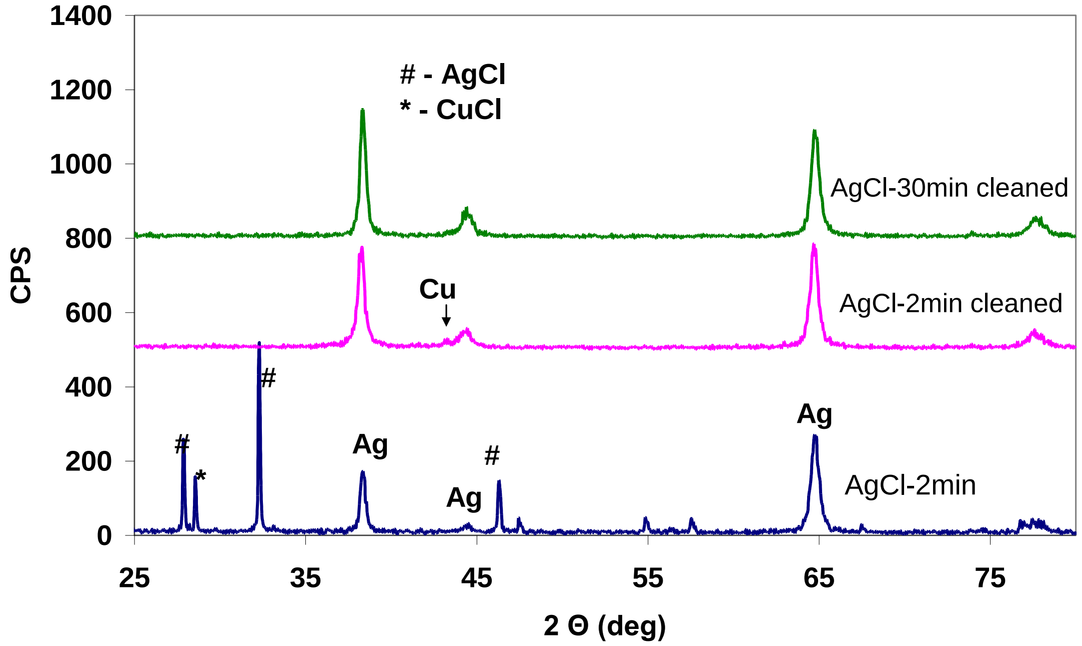


Figure 3. Comparative XRD diffractograms of the AgCl aged silver coupons before and after galvanic cleaning treatment

3.2 Ag_2S tarnishing and galvanic cleaning

Acanthite and chlorargyrite are the two minerals most often reported to be present in silver corrosion layers. The presence of these compounds and the essential absence of sulfate, nitrate, carbonate, or organic salts of silver are shown to be a natural consequence of the thin aqueous layer chemistry that occurs on silver in humid environments. The primary atmospheric agents responsible for the degradation are identified as H_2S, COS, particulate chloride, and possibly HCl, all acting in the presence of moderate to high humidity. Gaseous hydrogen peroxide, which is sometimes present, strongly accelerates silver corrosion. Acanthite is more difficult to form in solution than chloroargyrite because it contains two silver atoms, but silver is known to be less sensitive to chlorine than to sulphur [18]. To facilitate acanthite formation on the silver surface, silver coupons were immersed in hot Na_2S solution for 2 to 60 min. In that case silver suffers attack by dissolved oxygen and present sulphide species according to reaction (5):

$$4Ag_{(s)} + 2HS^{-}_{(aq)} + O_{2(g)} \leftrightarrow 2Ag_2S_{(s)} + 2\,OH^{-}_{(aq)} \qquad (5)$$

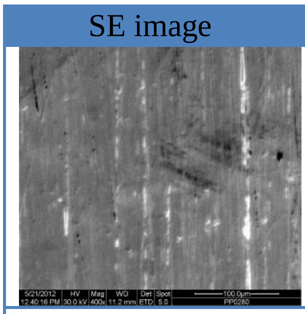
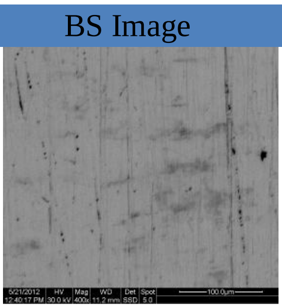
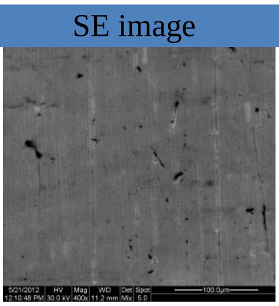
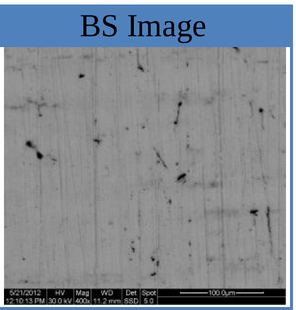
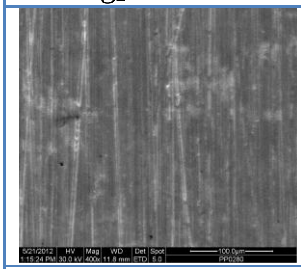
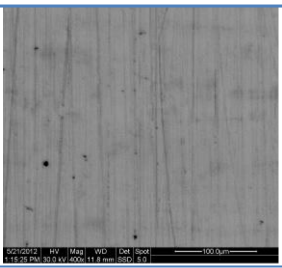
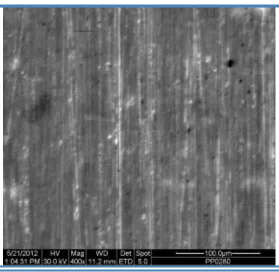
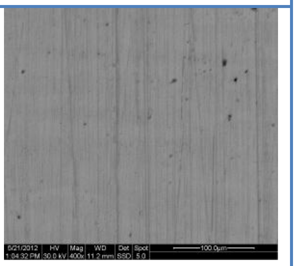
Silver sulphide formation was evident by coupons' colour change from yellowish–brown, for two minutes immersed coupons, to iridescent blue–black for longer immersions. This was also confirmed by SEM–EDS analysis where sulfur was detected at 0.5wt.% and 1.5wt.% on the surface after 2 and 30 min of immersion. The formation of silver sulphide may simulate post–burial degradation of archaeological silver objects (Table 5). Table 6 summarizes some SEM images of the Ag_2S tarnished as well as galvanically cleaned silver coupons.

The BS electron images and EDS analysis show the separation of copper and silver with the formation of copper "islands" (dark–grey areas) dispersed on the silver alloy surface. The presence of the copper "islands" in the silver alloys is a common feature of the silver–copper alloys due to the low solubility of Ag in Cu and vice versa at room temperature [19]. The occurrence of the copper and silver separation is always observed on a micro–scale in archaeological silver coins as well as macroscopically on coin surface as it has been reported by Ingo et al. [20].

Table 5. EDS map analysis of the Ag_2S tarnished silver coupons for 2 and 30 min before and after galvanic cleaning treatment

	Ag (wt.%)	Cu (wt.%)	O (wt.%)	S (wt.%)
Before Galvanic Cleaning				
Ag_2S–2 min	91.2	7.2	1.1	0.5
Ag_2S–30 min	89.3	8.0	1.2	1.5
After Galvanic Cleaning				
Ag_2S–2 min	89.2	7.4	3.4	-
Ag_2S–30 min	88.4	7.7	3.9	-

Table 6. SEM images of the Ag_2S tarnished silver coupons for 2 and 30 min before and after galvanic cleaning treatment

SE image	BS Image	SE image	BS Image
			
Ag_2S–2 min		Cleaned	
			
Ag_2S–30 min		Cleaned	

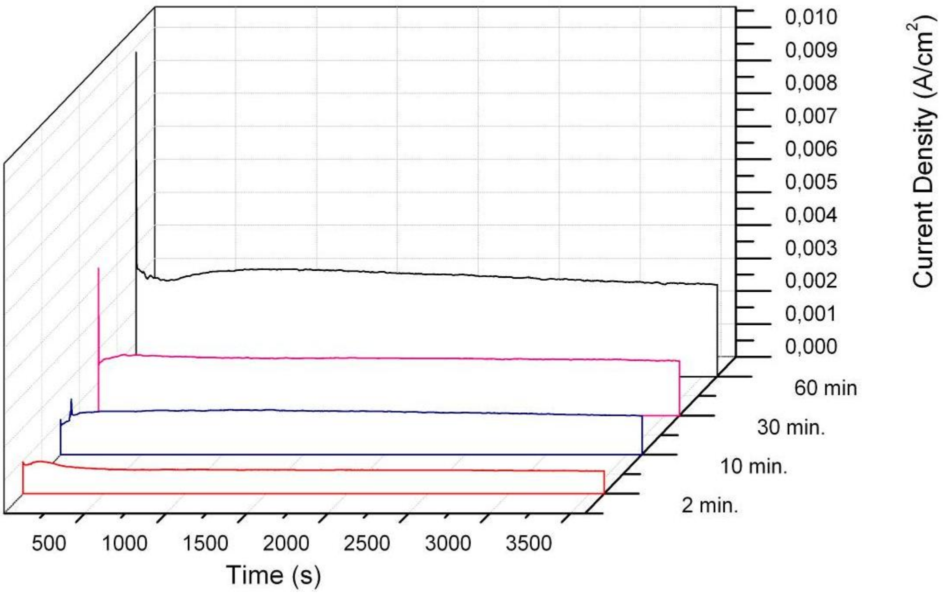


Figure 4. Galvanic current between Ag_2S tarnished silver coupons for 2–60 min and aluminum anode in 5wt.% Na_2CO_3 solution

Ag_2S–aged silver coupons were also galvanically connected to an aluminum electrode in 5wt.% Na_2CO_3 solution and the galvanic current was measured for one hour (Fig. 4). Long term current densities, of the order of 0.5–2 mA/cm^2, governed by hydrogen reduction kinetics were observed for all samples. They were 5 to 10 fold smaller than the one observed for AgCl aged silver. Very short time, current transients of 1–10 mA/cm^2, consistent with Ag_2S cathodic reduction, were indicated according to reaction (6):

$$Ag_2S_{(s)} + 2e^- + 2H_2O \leftrightarrow 2Ag_{(s)} + H_2S_{(g)} + 2\,OH^- \qquad (6)$$

Higher transients correspond to the depletion of the thickest Ag_2S layers. Although silver sulfide is stable in an alkaline solution and reduction is not thermodynamically favorable, the reaction takes place and results in the rapid depletion of these layers and apparent silver cleaning.

$$Ag_2S_{(s)} + 2e^- \leftrightarrow 2Ag_{(s)} + S^{2-} \qquad E^\theta = -0.71\ V \quad (7)$$

However, after the cleaning of heavily tarnished samples (immersed for 30 and 60 min) some small quantities of sulfur (~0.3wt.%) are detected on the surface by EDS analysis, and the colour is changed to light yellowish.

4. CONCLUSIONS

A reference sterling silver sheet alloy has been employed for carrying out two different accelerated degradation tests to simulate in the best possible way, the specific corrosion conditions of the silver objects. It was found that acanthite is more difficult to form in a solution than chloroargyrite, but silver is known to be less sensitive to chlorine than to sulphur. A galvanic couple between aged silver coupons and an aluminum anode results in the noble Ag acting as the cathode while the aluminum undergoes transpassive dissolution. The appearance of the short–time transient current is consistent with silver corrosion products reduction. The rapid depletion of these layers results in apparent silver cleaning. Long term galvanic current is governed by hydrogen reduction kinetics. After the cleaning of AgCl aged silver coupons a matt gray, porous silver layer has been created, which can be easily scratched from the surface. The chloride presence has not been identified, while after the cleaning of heavily Ag_2S tarnished samples some small quantities of sulfur (~0.3wt.%) are detected on the sample surface.

The use of SEM–EDS and XRD analytical techniques has provided good insight into the nature of the created surface corrosion and reduction products after cleaning treatment. The knowledge gained from detailed examination of such reference coupons can be very useful in determining the optimum procedure to restore and conserve archaeological silver objects.

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