The influence of gaseous pollutants in silver artifacts tarnishing.

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Abstract:

The present work aims to study the effect of the common gaseous pollutants on silver artifacts corrosion. The study will be carried out manufactured coupons of silver alloy (91 silver, 9 copper) which have chemical composition similarly to ancient Egyptian silver artifacts. These coupons will be exposed to gaseous pollutants of each individual gas; such as Sulfur dioxide, Nitrogen dioxide, Carbon dioxide, Hydrogen sulfide and Chlorine. The exposure period will be four weeks in a climate chamber with gas concentration 10 PPM. After test Examinations by SEM and PM were used to evaluate the effect of each gas and description the morphology of the corrosion layers. Results revealed that all gases reacted with the surface except carbon dioxide. Formed tarnishing layers varied in coverage and density rate. Corrosion products are analyzed by XRD and results were revealed Ag_2S, $AgCl$, Ag_2SO_4 and Ag_2O as corrosion products.

Key-Words: - Silver, artifacts, atmospheric corrosion, gaseous pollutants.

1 Introduction

Archaeological silver and its alloys have relatively high resistance to corrosion products in the atmospheric environment compared to copper and iron objects. But in the presence of humidity and gaseous pollutants - special Sulphur containing pollutants - Silver is susceptible to tarnish and deterioration occurs. Many corrosion products such as Ag_2S, Ag_2SO_4 and $AgCl$, have been identified on silver objects either in museum environment (displayed in cabinets and stored in depositories) or extracted from the burial environment. Silver objects corrosion in the atmospheric environmental attributed to the water layers on the surface which provide the reaction of atmospheric gases ionic such as chloride anions, sulphates, carbonates and organics with metallic surface and lead to the metal dissolution [20].

Among the family of ancient metals, the fewest studies on the laboratory and field exposure of the gaseous pollutants were presented to silver. Previous lab exposure tests often focused on silver tarnish due to Sulphur containing pollutants [1-6] these Studies have been agreed in their results which can be summarized in the formation of silver tarnish as black layer consisting of Ag_2S as major corrosion product and Ag_2SO_4 in a negligible quantity. Few lab exposure studies have been presented to impact other gaseous pollutants such as Cl, NO_2, and CO_2 but results were different and varied. The differences were as follow:

Results of Previous studies indicated that nitrogen dioxide is not considered a corrosion factor of silver because silver does not react with it, but it only acts as an accelerated factor of silver tarnish [7, 8, 9, 10, 11] even though Previous study was found silver nitrate Ag_2NO_3 as corrosion products in tarnish film of exposed silver to 1.2 ppm NO_2 for 40 hours [1].

Also Ag_2SO_4 as corrosion product was observed on silver coupons in field exposure [12] although the studies indicated that Silver sulfate (Ag_2SO_4) forms only in artificially high levels of sulfur dioxide [9, 11, 13, 14].

Silver is sensitive to chloride (Cl^-) and silver chloride will be formed as a result of the interaction [15, 10, 11, 14, 7, 9, 16]. Also this does not agree with results revealed that silver chloride compound was not identified on surface film of silver coupons after Exposure in an ASTM B117 salt spray chamber [17] and this compatibility with previous studies mentioned that silver does not react directly with chlorine gas and the presence of silver chloride as corrosion product due to burial in a chloride rich environment [18, 19].

Although Ag_2CO_3 is distinguished as corrosion product of silver as result of the interaction with CO_2, and although CO_2 is abundant in the ambient environment of silver artifacts, however - to our knowledge - did not presented lab. Exposure study of CO_2 with silver, Also Ag_2CO_3 has not been detected as corrosion product on the silver artifacts. Ag_2CO_3 was identified one year ago in field-exposure study on the Ag coupons exposed to various outdoor environments and the compound was detected only in one site which distinguished above the temperature inversion layer [20], So Very little is known about the formation mechanism of Ag_2CO_3 Such as it is expected only in strong alkaline solutions [21].

Therefore, in this study, the effects of gases (NO_2, Cl, CO_2) on silver will be presented as a laboratory exposure and compared with previous studies. Also they did not take sufficient laboratory studies although they were common gaseous pollutants in outdoor and indoor atmospheric environment, also hydrogen sulfide and sulfur dioxide were chosen as main gases in silver tarnish and lead to silver sulfide which was often observed as corrosion product of silver.

2. Experimental procedures:

2.1. Coupons preparation.

Silver coupons should be similar for archaeological silver of ancient Egypt civilization, different concentrations were found in Ancient Egyptian Silver, elemental analysis of a number of Egyptian silver artefacts was showed that 10 objects concentration between 83 to 90%, and 19 objects of silver ratio ranged from 90 to 95% [22, 23]. Also analysis of Babylonian coins from silver copper alloy were about 87–90% purity [21]. So that a composition of coupons was Ag 89.4% and Cu 10.5%. This concentration was not artificial available and was manufactured by alloying a mixture of silver (pieces from the pure silver) with pure copper pieces. The coupons were made by direct addition of silver and copper in a crucible [24]. fig. 1. The dimensions were (3 cm × 5 cm × 0.08 cm) Fig. 2. XRF analysis used to determine the Composition as in fig. 3.

Thin thickness of coupons about 8 m will be suitable and similar to silver artifacts thickness, because most the silver artefacts were manufactured to thin sheets whether by cold-working or casting in moulds such as thin sheets for royal garments, hollow statues, jewellery items, funeral items, Household items of everyday life such as, spoons, jugs, cups, vessels, pots, covered wooden object, bowls and Other usages, so that Successive processes of hammering and ductility with the annealing on alloy rod to obtain thin thickness about .8 m. five new coupons were used For each gas test, a hole was drilled in each sample for suspension in the chamber middle [21].

2.2. Design and Preparation of climate chamber test.

Climate chamber was designed according to ASTM [45]. It is made of 1000 cm diameter Perspex cylinder. The humidity was controlled gradually by the cup of saturated salt solution inside the chamber, the approximately 85%RH was obtained by a saturated solution of potassium chloride [46] and the chamber was only opened to remove coupons. Heating of the air inside the chamber is done by a cartridge heater, the air inside the chamber is continuously mixed by a fan, which was suspended from the ceiling of the chamber, the temperature and relative humidity inside the chamber are continuously measured by dataloger device [47, 48]. A few studies were presented on the silver deterioration tests inside climate chamber, these studies used two types of the deterioration factors: high relative humidity [9, 44] and gaseous pollutants in presence relative humidity [25, 44, 1]. Most studies of silver deterioration were used corrosive solutions as deterioration factors, such as BaS 5 g/l solution for 24 Hours [18] and Na_2S were used as the tarnishing solution [9, 50]. Acetic acid solutions were used as simulation of emissions vapors in wooden cabinets and $CuCl_2$ 50 g/l for 20 min, and NaCl [50] were used of AgCl silver patina [18].

2.3. The test gases.

The gases for the test were as follows: Sulfur dioxide SO_2, Nitrogen dioxide NO_2, Carbon dioxide CO_2, Chlorine gas Cl and Hydrogen Sulphide H_2S. Those types were the most influence in deterioration of silver artefacts.

2.4. Test procedures.

Each five coupons were exposed to humidified air containing concentration 10 ppm of one gas only. The values of other factors were chosen after surveying 29 previous studies which considered lab exposure of ancient metals family (copper, bronze, silver, steel and lead) as shown in table 1. Their most experiments were performed at room temperature (22 - 25 C), and relative humidity between 80 - 90. There are the other two factors such as:
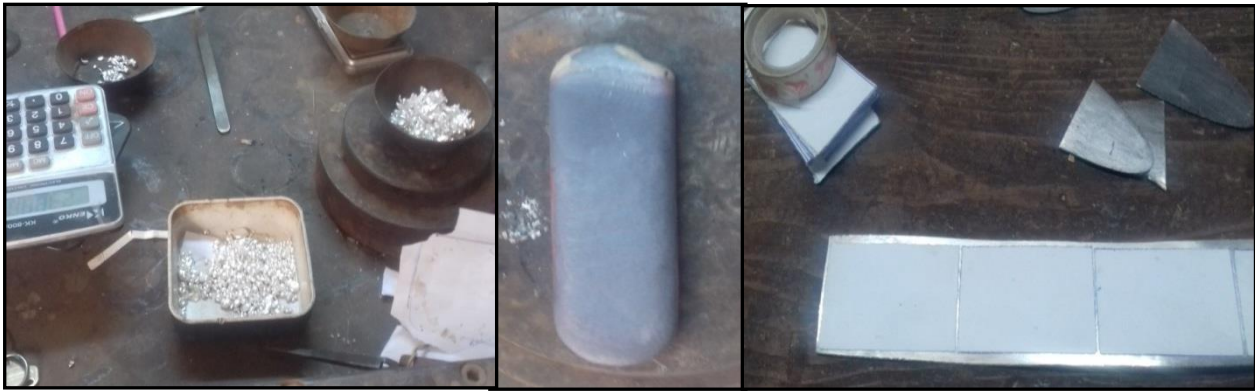
Fig. 1. Manufacturing to silver coupons, (a) pure silver pieces (b) shape of resulting rod after casting, (c) cutting coupons after ductility and hammering processes.

Fig. 2. Silver alloy coupons before the exposure.

Fig. 3. XRF of silver alloy coupons.

The gases concentration and the exposure period which were varied from study to another. So accelerated conditions parameters were as shown in table 2.

Cylinders 99.9 % concentration were used to obtain of CO_2, SO_2 and NO_2 gases, The gas flowed from cylinder into the exposure chamber after the calculation of flow and time of the required concentration. H_2S and Cl^- were prepared in lab, H_2S prepared by the reaction of hydrochloric acid diluted with ferrous sulfide (equation 1) [51] and Cl^- prepared by the interaction of concentrated Cl^- with manganese dioxide (equation 2) [52]. According to the law of Avogadro and Lussac can be calculated Volume which the required concentration of H_2S and Cl^- inside the chamber is occupied. Where Molecular weight (one mole) of any gas under standard conditions is occupied 22400 ml (the molar volume, equation 3) [53].
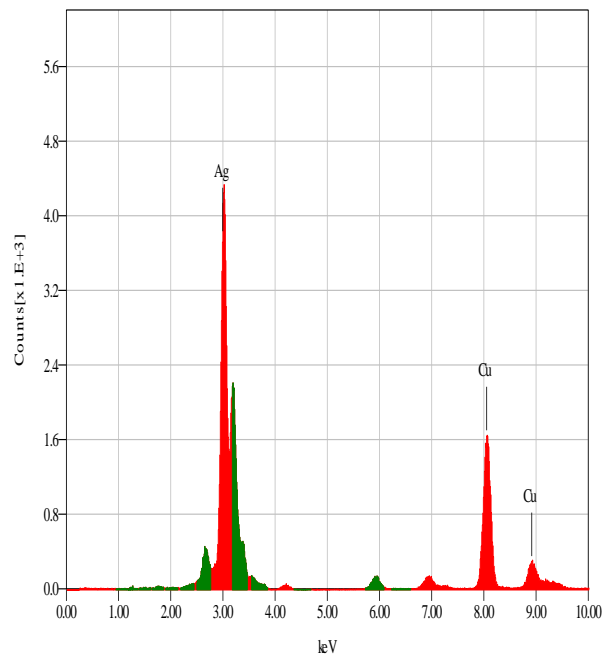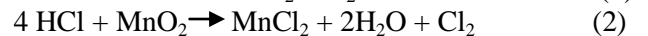
And by the calculated of molecular weight to H_2S equation (4) which occupied 22400 ml can be calculated volume of the required concentration of H_2S equation (5).

$$FeS + 2HCl \longrightarrow FeCl_2 + H_2S \qquad (1)$$
$$4\ HCl + MnO_2 \longrightarrow MnCl_2 + 2H_2O + Cl_2 \qquad (2)$$
$$1 \text{ mole of a gas at STP} = 22.4 \text{ liters of a gas} \qquad (3)$$
$$2X1+32 = 34g = 22400 \text{ ml} \qquad (4)$$
$$ppm\ (19\ mg/m^3) = X\ ml \qquad (5)$$

Gas syringe was used to get the required volume and injected it into inside chamber fig (4), the fan was used for mixing gases and its distribution inside the chamber.

Table 1. Summarizes lap exposure conditions to gaseous pollutants with ancient metals in the previous studies.

Ref.	Gas	time	Concentration	C RH	Coupons
[25]	(OCS), H_2S, (SO_2)	5 week	2.5 – 0.26 ppm 2.66 - 3.64 ppm	22 50	Silver
[26]	SO_2, NO_2	30 hours	10–22 ppm, 1.8 ppm	25℃ 80–90%	Tin
[27]	H_2S	22-77 days	50ppb, 2ppm	10, 30, 80, 40 %	Copper
[28]	(SO_2+NO_2)		75 ppb SO_2 + 120 ppb NO_2		Copper
[29]	Acetic and formic acid vapors	One, two and four weeks.	formic acid 160 ppb, acetic acid, 170 ppb, CO_2 350 ppm	22℃ 95%	lead
[30]	H_2S, NO_2, Cl_2	4, 10 days	10, 200, 10 ppb	30℃ 70%	Copper
[31]	Mixture of NO_2, SO_2, O_3		200 ppb SO_2, 200 ppb O3. NO_2 ppb	25℃ 80%	Copper
[32]	Vapor HNO_3	7 days	325 µg/ m^{-3}	25℃ 65%	Copper
[33]	Mixture of SO_2, H_2S		SO_2 75 ppb, H_2S 50 ppb	25℃ 75%	Copper
[34]	Mixture of SO_2, NO_2	10, 30, 60 hour	SO_2 75 ppb, NO_2 120 ppb	25℃ 75%	Copper
[35]	Formaldehyde, Acetic and formic acid	135 days	0.04, 0.4, 4, ppmv	25℃ 54 ,75%	Copper, lead
[36]	formic and acetic acid	21 days.	(10, 50, 100, 200 and 300 ppm)	30℃ 100%	Copper
[37]	HNO_3	2 weeks	(126 ppb)	25 65%	copper, zinc and steel
[38]	NO_2, NO_2+ SO_2	2 weeks	(800 µg/m^{-3}), (800 µg/m^{-3} +800 µg/m-3)	30℃ 90%	Zinc
[39]	SO_2	- 4 week	(10 ppm)	25 90%	copper
[40]	SO_2+O_3	- 4 week	(476 ppb + 500 ppb)	30 70%	Copper
[41]	NO_2+ SO_2	- 4 week	(200 + 3000 ppb)	25 90%	Steel
[42]	H_2S	- 4 week	(50-200 ppb)	25 80%	Copper

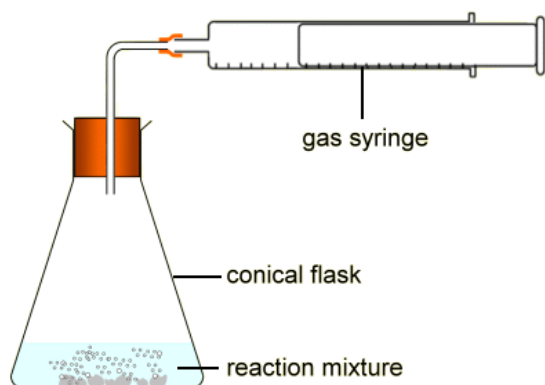| [43]	(SO_2+NO_2)	7, 14, 21 and 28 days	(200 and 800 μgm^{-3})	15, 25, 35 C) (50%, 70% and 90%).	copper
[44]	O_3	24 h	500 ppb	(0, 50, 90%)	Silver
[1]	NO_2, H_2S	40 hours 72 hours	1.2 ppm NO_2 100 ppb H_2S	25 75%	silver

Fig. 4. The syringe and the method of taking the required volume from the gas resulting from the interaction.

Table 2. Conditions and procedures of the test.

Period	T	RH	Concentration
8 weeks	25 C^o	85 %	10 ppm

3. Results and discussion.
3.1. Examination of the samples after the test.

The Coupons were examined after each test by Visual examination, Polarizing Microscope and Scanning Electron Microscope to identify the morphology and composition of the formed layer and evaluate the interaction between the coupons surface and the test gases. The investigation results revealed that all the coupons surfaces interacted with the gases from the first week except the exposed coupons to carbon dioxide. The interaction began as a very thin layer on the surface, and the surface appearance turned from light interference tones to a grey and, finally, black film. Also the tarnishing rate was increased with H_2S, Cl, decreased with SO_2, NO_2.

The reaction behavior inside the chamber and the growth rate of the tarnishing layer during exposure were similar among Cl, H_2S, and NO_2. From the first week the growth of layer was generally rapid, and was getting slower afterwards. The formed tarnishing layer, thickness, density and coverage of the surface differed among the test gases as shown in Fig. 5. H_2S coupons recorded the highest thickness, density and coverage of the formed layer. Also H_2S caused pitting in the metallic core. Cl coupons were completely covered by a uniform general dense layer of silver tarnishing. CO_2 coupons revealed very weak effect of gas. Slightly tarnishing layer with green spots were observed on the surface of NO_2 coupons. SO_2 coupons showed the least tarnishing layer and the reaction was very slow although humidity existed, the slow reaction of SO_2 with silver was mention in previous studies [28].

3.2. The analysis of corrosion products by x-ray diffraction.

The coupons were exposed to x ray diffraction to analyze the formed patina. This was showed many of corrosion products as in Fig. 7.

Silver sulfide (Ag_2S Acanthite): they were identified as abundant on silver artifacts. The reaction behavior between gas H_2S and the silver surface to form these products explains equations (6, 7).

$4Ag + O_2 + 2H_2S \longrightarrow 2Ag_2S + 2H_2O$ [54, 55] (6)
$2Ag + H_2S \longrightarrow Ag_2S + H$ [24]   (7)
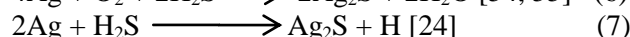
Silver chloride (AgCl Cerargyrite, chlorargyrite): In this case, the dominant theory in the interpretation of formation mechanism of chloroargyrite AgCl is the transformation of Ag_2O to AgCl as equation (8) [12, 15].
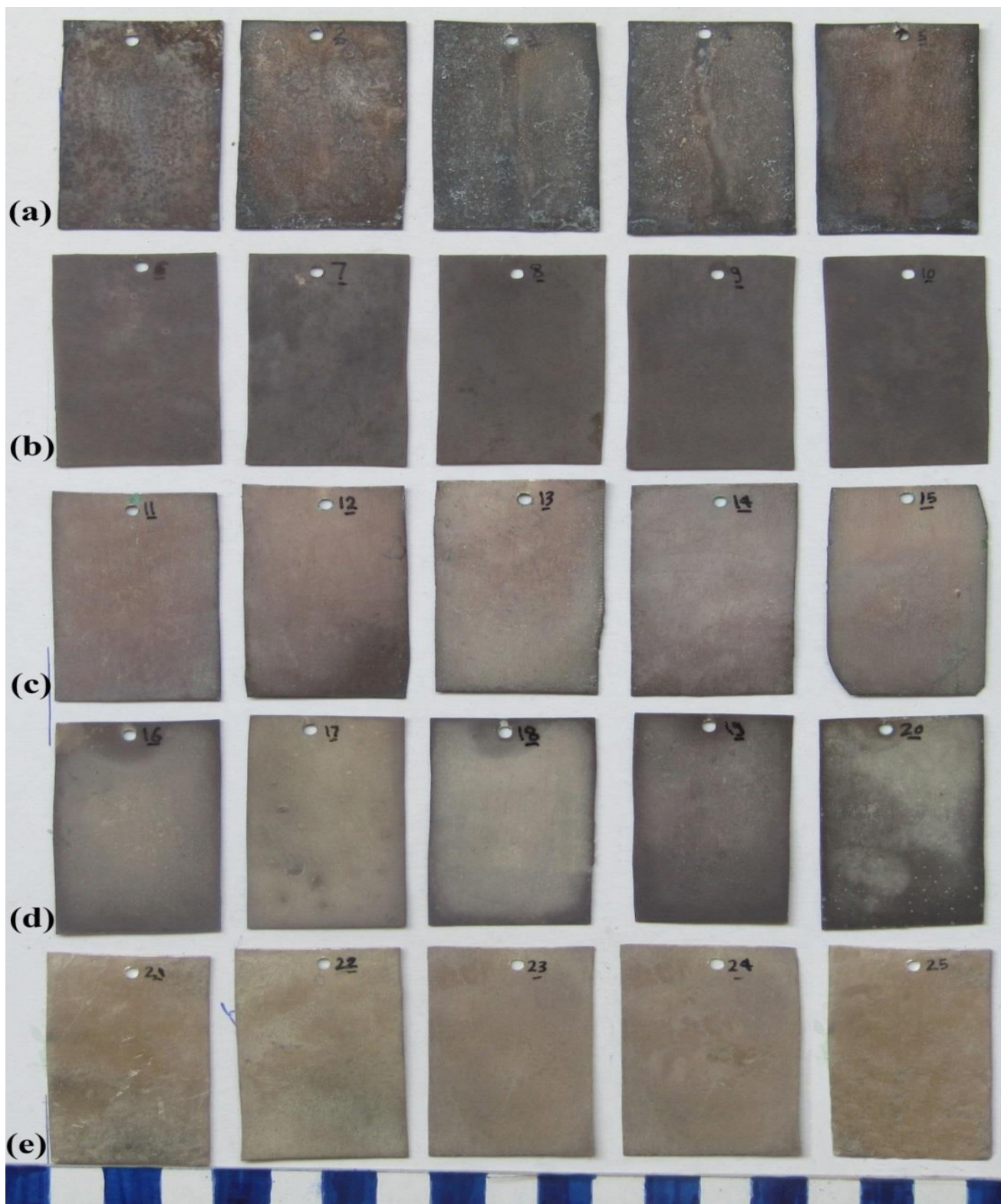
$Ag_2O + 2Cl^- + H_2O \longrightarrow 2AgCl + 2OH^-$ [12] (8)
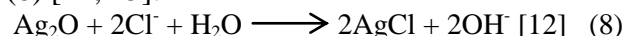
Fig. 5. The coupons after the test, (a) the coupons exposed of H_2S (b) the coupons exposed of Cl, (c) the coupons exposed of SO_2, (d) the coupons exposed of NO_2, (e) the coupons exposed of CO_2.
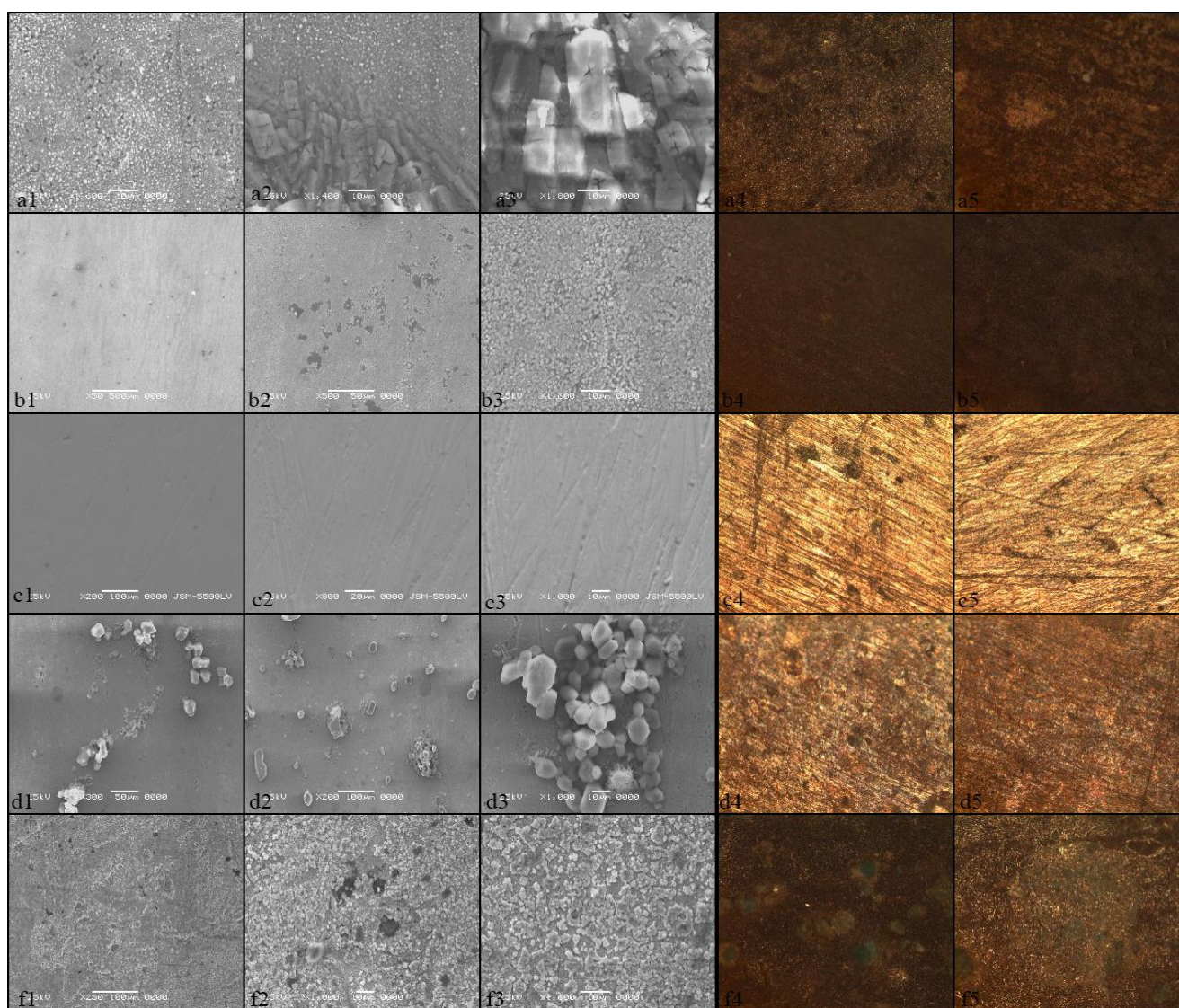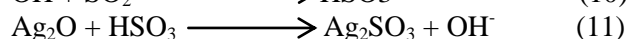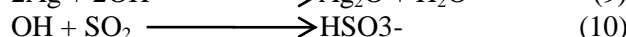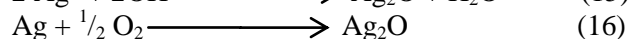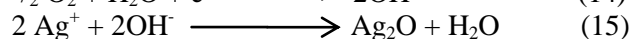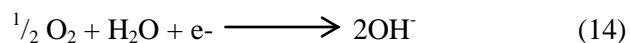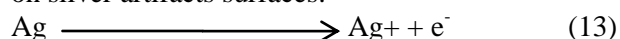
Fig. 6. Investigation by polarizing microscope x500 shows the most important characteristics of tarnishing layer on the surface such as H_2S coupons are covered by dense tarnishing layer (a1-a5). Cl coupons reveal a uniform and thick tarnishing layer (b1-b5). CO_2 coupons reveal very weak effect of the gas (c1-c5). SO_2 coupons reveal the crystal structure of product of tarnishing (d1-d5). Green spots on the surface of NO_2 coupons (f1-f5).

Silver sulfite (Ag_2SO_4): This product was identified in a previous study as corrosion product of silver 20 and the equations (9-12) were suggested for the mechanism of its formation on silver coupons surface.

$$2Ag + 2OH \longrightarrow Ag_2O + H_2O \qquad (9)$$
$$OH + SO_2 \longrightarrow HSO3- \qquad (10)$$
$$Ag_2O + HSO_3 \longrightarrow Ag_2SO_3 + OH^- \qquad (11)$$
$$Ag_2SO_3 \longrightarrow Ag_2SO_4 \qquad (12)$$

Silver oxide Ag_2O: Silver artifacts react with oxygen either by the electrochemical reactions in the presence of humidity (equations 13-15) or by chemical reactions in the absence humidity (equation 16). Therefore Ag2O and AgO are formed on silver artifacts surfaces.

$$Ag \longrightarrow Ag+ + e^- \qquad (13)$$

$$^1/_2 O_2 + H_2O + e- \longrightarrow 2OH^- \qquad (14)$$
$$2 Ag^+ + 2OH^- \longrightarrow Ag_2O + H_2O \qquad (15)$$
$$Ag + {}^1/_2 O_2 \longrightarrow Ag_2O \qquad (16)$$

Silver ammine nitrate ($Ag(NO_3)_3(NO)_3$): previous studies of filed and lab. exposure were identified only one product ($AgNO_3$) from nitrates anions as corrosion products on silver surface, Therefore this compound was expected of NO_2 gas, but analysis showed Silver ammine nitrate ($Ag(NO_3)_3(NO)_3$).

Copper Nitrate Hydroxide (Rouaite, $Cu_2(NO_3)(OH)_3$): Silver and copper are the coupons alloy elements, the formation of Rouaite corrosion product is contributed to selective corrosion of copper by the interaction of cu (as the main alloying element) with NO_2 gas.
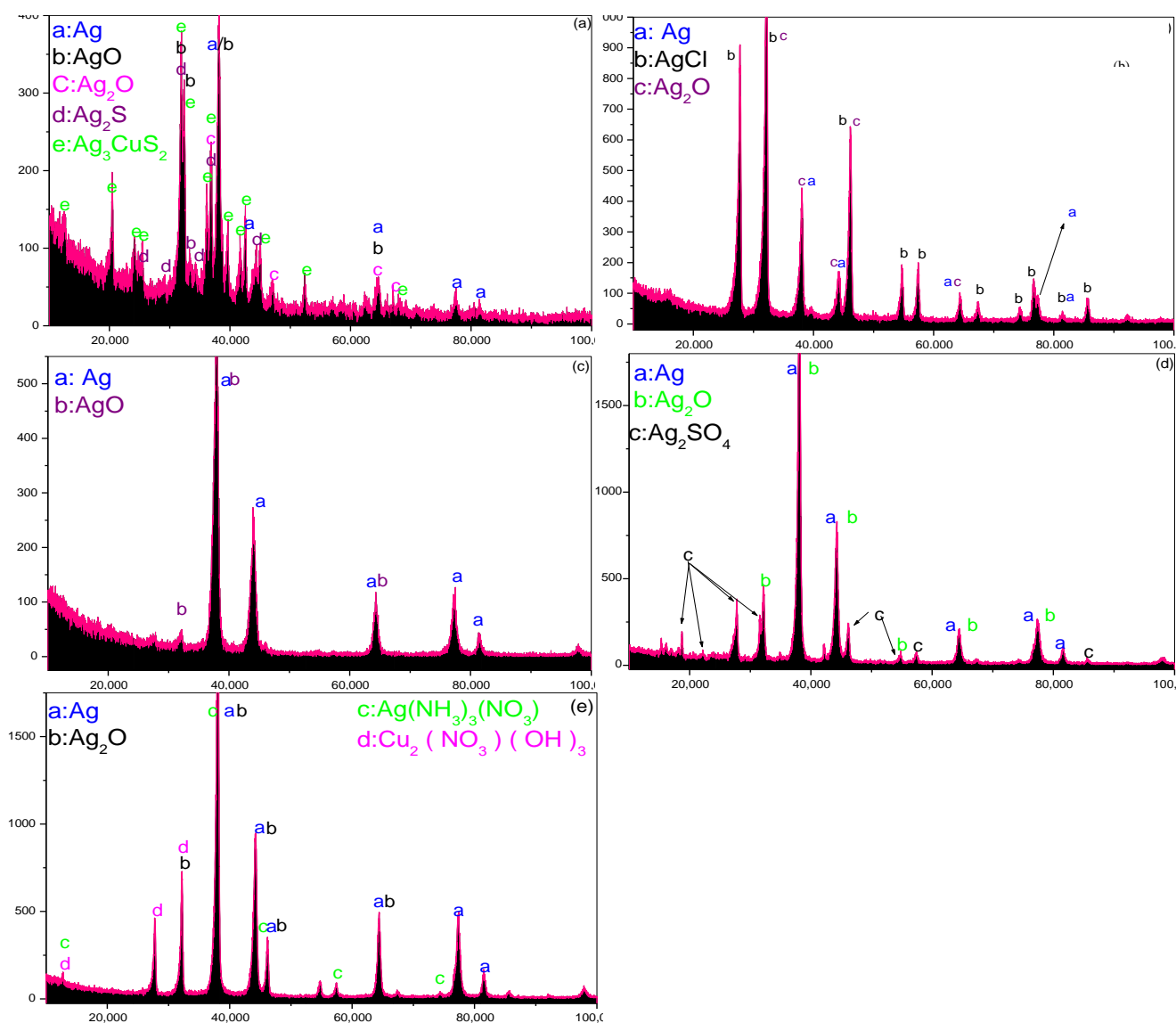
Fig. 7. XRD patterns of tarnishing layers of the coupons, (a) tarnishing of H_2S, (b) tarnishing of Cl, (c) the coupons of CO_2, (d) tarnishing of SO_2, (f) tarnishing of NO_2.

4 Conclusion

Silver in atmospheric environmental and presence humidity are susceptible to formation of surface tarnishing layer. The tarnishing is formed not only in the presence of Sulphur containing pollutants but also in presence other gaseous such as Cl and NO_2.

Except the coupons of CO_2, all the test coupons were exposed to tarnishing layer which was formed on the surface as a blackish thin film caused by the interaction of the metal surface with test pollutants. But highest layer in density and tarnishing was to H_2S gas.

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