THE TARNISHING CONUNDRUM OF SILVER

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Abstract

This paper presents an understanding of the tarnishing of silver by examination of the mechanisms of the processes involved. The paper outlines the fundamental processes of the corrosion and oxidation of silver, and its relation to the corresponding properties of other metals. Tarnish on the surface of silver is deemed unsightly because it removes the brilliance and reflectivity of a pristine silver surface, as it turns black over time, usually unevenly. The composition of the tarnish is ultimately silver sulphide (Ag_2S), because this compound is very stable. However, tarnish may also contain other compounds of silver, particularly silver chloride, and silver oxide. The processes leading to tarnishing are strongly influenced by many components of the environment. Mechanisms by which the sulphide is formed on the surface of the metal are discussed. Silver sulphide forms because it is the most stable oxidised compound of the metal under normal atmospheric conditions, even under low pressures of sulphur-containing gases in the atmosphere. This means that the normally passivating oxide which should cover the metal is converted slowly to the sulphide. The mechanisms and processes by which this occurs are discussed.

Introduction

The long-known and widely studied tarnishing of silver and its alloys has its origins in antiquity. Silver metal has been used both as a functional material and as a decorative metal for millennia. As a functional material in antiquity its use in coinage and in utilitarian vessels over very many centuries contrasts its modern application as electron conductive interconnects in microcircuits. As recently as the reign of George (V), the 3d coin in common circulation was made of silver: sterling silver (containing 92.5% Ag) used in earlier coinage was reduced to an alloy containing 50% Ag in 1920. The phenomenon of tarnishing interferes with all aspects of its application in both areas.

The problem of tarnishing and its challenges can be divided into two broad practical categories, which present different approaches. In the first, artefacts from history (recent or ancient) already in existence will always remain of importance, and are under continuing study in archaeology and archeometry: these require preservation and protection indefinitely. The oldest such artefacts appear to date from ca. 4000BC (from ancient Sumer). Tarnishing can reduce the lifetime of some artefacts, although the tarnish itself is remarkably protective. The progress of tarnish in relatively benign environments can be very slow. Tarnishing does however, progressively degrade the surface detail and surface finish. Simply cleaning tarnish from the surface physically or chemically as it forms is not a solution to the problem, since many such methods remove the surface carrying the tarnish, and the item then re-tarnishes on further exposure. Such items require surface protection and preservation in their original state, without significant modification. In the second category, items that are of no historical interest, and are perhaps, yet to be made, offer a chance to develop systems where tarnish resistance can potentially be built into the metal or into its surface. For example, electronic microcircuits, which use silver as interconnect material (because of its high electron conductivity) can fail under formation of tarnish. Alternative copper interconnects can sometimes be silver-coated and suffer the same problems. Because of the very small dimensions of interconnects, relatively little tarnish-forming corrosion can (and does) cause circuit failure. This problem is unique to the very tiny systems that are used extensively in electronic circuits. (Copper itself as interconnect material also suffers the same problem, and more sensitively.) There are further ramifications of this particular problem (hence its mention in the present context). Silver, like other interconnect materials, can form "whiskers" (1,2) under the high electric fields which exist in microcircuits in service: such whisker formation is enhanced by corrosion and tarnish formation, presumably by focusing the electric fields in specific areas. Whisker growth causes component failure by forming electric short-circuit paths. The challenge lies separately in these two areas: however, there is potential overlap in the possible approaches to tarnish control or protection.

Tarnishing of silver can in fact, reduce the functionality of systems in which the metal performs a functional purpose. Apart from the electron conductors in electronic circuitry, use of the metal as a mirror surface in items such as telescopes is also degraded by tarnishing, and such surfaces require protection to prevent this. The problems of tarnishing can also affect the use of nanoparticulate silver (Ag particles of nanometre dimensions, sometimes defined as particles of diameter less than 100 nm, but can be very much less), described below. Such particles have application in diverse areas, such as catalysis and medicine.

With the exception of gold, and some of the platinum group metals, silver is the most noble of the easily corroded metallic elements. Most metals, which appear not to corrode, or corrode very slowly, are much less noble than silver, and this fact requires detailed understanding. The very familiar "electrochemical series", which is an assessment of the relative nobility of the metallic elements of the periodic table, does not even begin to explain that fact, despite its widespread, often erroneous use in the field of corrosion and protection. The thermodynamics of the electrochemical series is in itself perfectly sound, but its application often exceeds its useful boundary. That series deals with the thermodynamics of the metal in equilibrium with its dissolved cation only. Anything more than that cannot be handled by this simple concept. In fact, most metals in practice require the phenomenon of "passivity" against corrosion to minimize corrosion, and silver is no exception to this. To understand these phenomena, requires an understanding of corrosion as well as an understanding of passivity and passivation. Metals passivate because of the formation of an intervening oxide film which is protective, and which form as a direct consequence of the oxidation reaction. Not all oxides formed on the surface passivate the metal however, and detailed understanding of this is necessary. The ability for an oxide which forms on the metal to passivate that metal depends on the properties of that oxide, as well as on the mechanism of its formation.

Tarnishing of silver is a corrosion process in dry or moist air, in which the corrosion product is a solid oxidised compound of the metal. The reactivity towards many components of the environment, as well as the sensitivity of silver compounds towards light (visible and ultraviolet) contribute to the degradation corrosion product as well as to its unsightliness. The phenomenon of tarnishing is synonymous with that of patination: the only significant difference is the physical appearance of the corrosion product. In general terms, tarnishing of silver is an undesirable property, partly because it is regarded as unsightly, but also partly because it consumes the surface of the metal: the latter is not normally a major issue, but can become major if the tarnish is removed repetitively. By contrast, patination of copper is often regarded as desirable because it is regarded as attractive when green in colour, and because it is a semi-protective. Green copper roofing materials are readily found through many of the cities of Europe. Patination of copper does not however, always form a green surface, and can often be found in a dark or blackened form.

It is important to point out two features of tarnishing of silver, which are fundamental to the problem.

1. In air, wet or dry, silver forms a surface oxide film very rapidly indeed, in common with very many metals in service. The formation of the oxide is protective against further oxide formation.

2. Suggestions that the silver surface is not oxidized by atmospheric oxygen at ambient conditions, but rather, that carries a "chemisorbed" layer of molecular or atomic oxygen (3,4) is unlikely to be correct. It is the formation of an oxide film that satisfies the thermodynamics of silver. However, whether that resembles a 1- or 2-monolayer thickness of oxide film, or a thicker form, is a more moot point. In fact, the very suggestion must be called to question, since at least one of the relevant papers (4) uses temperatures of 750 and 800 °C for the exposure. The relevant thermodynamics shows that the oxide of silver, Ag_2O is thermodynamically unstable at such high temperatures, and would decompose to Ag and O_2 already at much lower temperatures.

3. Although tarnishing is usually attributed to the formation of black silver sulphide (Ag_2S), silver oxide (Ag_2O) as an ordinary chemical is also black or dark brown. Since silver oxide is known to be formed on the surface of the metal, it raises the question as to why the tarnish layer is so frequently (but not always) found to be composed largely of Ag_2S. The answer to this lies in the thickness of the film formed. In normal air (dry or wet), silver retains a bright lustre despite the fact that Ag_2O forms very quickly. That oxide is protective, and grows only to very low thickness. It very high degree of protectiveness is probably due to the formation of an amorphous structure, with no crystallinity, and is so thin, that it cannot have colour. There are many metals that "passivate" in this way, and the thin oxide that forms does not have the colour of its crystalline counterpart. For example, Cu is passivated by formation of cuprous oxide (Cu_2O), again as a very thin, colourless film; However, bulk crystalline Cu_2O is dark red, which is not seen on passive copper. Nevertheless, Cu passivates well in air (but also patinates). Chromium passivates by formation of a very thin film of Cr_2O_3, and the metal maintains a bright metallic lustre in air over very long periods. However, as a bulk material, Cr_2O_3 is dark green.

4. It is a fact that tarnish surfaces are often found to consist of some mixture of silver sulphide (Ag_2S) and silver chloride (AgCl), with some oxide as well (5-11). The relative amounts found by analysis vary hugely amongst the papers published in the field. Some reports show the presence of additional compounds, including silver sulphate (Ag_2SO_4) and some organic silver compounds have also been identified.

These differing observations are not actually contradictory, and they are not surprising: indeed, this variation is expected. The composition of the tarnish depends strongly on both the composition of the environment used, as well as the immersion time (in addition to that of the silver composition). Indeed, many aspects of the environment composition are known to affect tarnishing. The reasons for this should become apparent below.

Thermodynamic properties of silver compounds relevant to tarnishing

The composition of the tarnish layers on silver in air has been identified many times. It is often found to consist mainly of the sulphide (Ag_2S) with some chloride (AgCl) and oxide (Ag_2O), and we deal only with these here. Some reports of more sulphide than chloride or vice versa, and the presence of oxide etc are fully consistent with differences in composition of the atmosphere, and with different exposure times. The problems of tarnishing are easily quantified when it is realised that both silver sulphide and silver chloride are very stable compounds. Listed in Table 1 is a set of standard chemical potential, μ^0 (also termed the standard free energy of formation, ΔG^0_f) for some compounds relevant to tarnishing of silver. The reader should realise that Table 1 is not an exhaustive list, but rather relates to some reactions considered relevant to tarnishing, which involve sulphur-, chlorine- and oxygen-containing components of the atmosphere.

Compound	Standard chemical potential (μ^0), kJ/mol
Ag_2O	-10.837
Ag_2S (α)	-40.25
Ag_2S (β)	-39.162
AgCl	-109.704
H_2O (l)	-237.191
H_2O (g)	-228.614
H_2S (aq)	-27.363
H_2S (g)	-33.020
SO_2 (g)	-300.369
SO_3 (g)	-370.410
COS (g)	-165.7
HCl (g)	-95.265
HCl (aq)	-131.168
Cl^-(aq)	-131.168
CO_2 (g)	-394.39
CO (g)	-137.16

Table 1
Standard chemical potential (standard free energy of formation) at 25 °C of some compounds relevant to the tarnishing of silver. Data from references 12 and 13, with the energy converted to joules.

By using the thermodynamic data, it is easy to see that the reactions forming silver sulphide (and silver chloride) from the metal or from its oxide show a strong negative standard free energy change, favouring formation of that sulphide. The following reactions must be considered in relation to the common gaseous sulphur compounds in the environment. The standard free energy of each of these reactions, ΔG^0, which has been calculated from published data using the standard chemical potentials (see Table 1) of the relevant compounds (12,13), are given in Table 2.

$2Ag + H_2S \rightarrow Ag_2S + H_2$ (1)

$2Ag + COS \rightarrow Ag_2S + CO$ (2)

$2Ag + 3H_2SO_3 \rightarrow Ag_2S + 2H_2SO_4 + H_2O$ (3)

$Ag_2O + H_2S \rightarrow Ag_2S + H_2O$ (4)

$Ag_2O + COS \rightarrow Ag_2S + CO_2$ (5)

$Ag_2O + 4SO_3^{2-} + 2H^+ \rightarrow Ag_2S + 3SO_4^{2-} + H_2O$ (6)

$2Ag + SO_2 \rightarrow Ag_2S + O_2$ (7)

$Ag_2O + 4SO_2 \rightarrow Ag_2S + 3SO_3$ (8)

$2Ag + 2HCl(g) \rightarrow 2AgCl + H_2(g)$ (9)

$Ag_2O + 2Cl^-(aq) + H_2O \rightarrow 2AgCl + 2OH^-(aq)$ (10)

$2AgCl + H_2S \rightarrow Ag_2S + 2HCl(aq)$ (11)

$2AgCl + H_2S \rightarrow Ag_2S + 2HCl(g)$ (12)

$2Ag + \frac{1}{2}O_2 \rightarrow Ag_2O$ (13)

reaction number	ΔG^0 kJ/mol	atmospheric pressure of reactant gas, bar *	atmospheric pressure of product gas, bar	ΔG kJ/mol	minimum reactant gas pressure required for Ag_2S (reaction 9: HCl; reaction 13: Ag_2O) to form, bar
1	-7.23	10^{-9}	5×10^{-7}	+8.17	2.8×10^{-8}
2	-11.71	5×10^{-10}	2.5×10^{-7}	+3.69	2.2×10^{-9}
3	-146.11				
4	-225.01	10^{-9}	0.01**	-185.08	3×10^{-40} ***
5	-258.50	5×10^{-10}	0.0035	-219.45	1.7×10^{-48} ***
6	-657.54				
7	+260.12				
8	+60.83				
9 (gas)	-28.878	10^{-9}	5×10^{-7}	+37.863	(0.24 for HCl)
9 (aq)	+42.928	(aq)			
10	-260.83				
11	-50.158	10^{-9}			
12	+21.944	10^{-9}	10^{-9} **	-29.399	1.4×10^{-22}
13	-10.387	0.209		-8.448	2.28×10^{-4} for Ag_2O

Table 2
Thermodynamic characteristics of some reactions of silver in the atmosphere which lead to the formation of Ag_2S and AgCl.
*: assumed atmospheric pressures of H_2S and COS from published literature (5, 9,14)
**: assumed partial pressure for H_2O or HCl *vapour*.
(*** Note that very low pressures of gases calculated thermodynamically are not quantitatively meaningful, because the very basis of molecular thermodynamics requires a statistically large number of molecules: pressures as low as 10^{-40} bar cannot have that. Indeed, such pressures are themselves, in fact, meaningless.)

In the list above, reactions 1, 2 and 3 are with metallic silver. Reactions 4, 5 and 6 are reactions of silver oxide. Both the metal, and the oxide are reactive, but the bare metal reacts at pressures of S-containing gas a little higher than those considered to be about average, as indicated in the table. Some of the reactive sulphur species considered here are gas phase, and some are dissolved phase, the latter being of importance where the atmosphere is humid. Included also, is the gas phase compound carbonyl sulphide (COS). Carbonyl sulphide also occurs naturally in the environment at very low partial pressure, of *ca*. 0.5 ppb (5,14). Using the published values of the standard chemical potentials for the relevant compounds, the standard free energy of reaction, ΔG^0, at 25°C for each of the reactions shown is as shown in Table 2.

Whilst the standard free energy of reaction, ΔG^0 is widely used as a thermodynamic means for defining the direction of a chemical reaction, this is strictly speaking, wrong. The *standard* free energy of reaction is in fact a thermodynamic measure of the equilibrium constant for that reaction, and that is all: it does *not* define the reaction direction *per se*. To estimate whether the reaction in fact proceeds from left to right or vice versa from such thermodynamic data requires calculation of the *actual* free energy of reaction (not the standard free energy), and this involves applying the actual pressures of the reactive gases (not the standard pressure), and actual concentrations of dissolved species (not the standard concentration). The matter is important for the reactions of silver considered here. That is seen already by the fact that the pressure of oxygen in the atmosphere is overwhelmingly greater than that of the sulphur-containing gases. To put this into context, Table 2 presents the calculated driving force, ΔG, which is the free energy change of some of the reactions using the commonly listed compositions of some gases in air (5,9,12,14,15). The table also lists the minimum atmospheric partial pressures of the sulphur gases (H_2S and COS) calculated thermodynamically, which are necessary to cause formation of Ag_2S. It is noted that these minimum pressures/concentrations are all very low, some far below what could be measured experimentally. (Indeed, some pressures so low that they are meaningless, thermodynamically and practically.) This is important. Where the minimum pressure of the aggressive gas (required to react) is very low, it means that any pressure of that gas will cause reaction, however slow that reaction may be. We can rationalize a number of important facts.

1. The reaction of metallic Ag (ie, free of surface oxide) with H_2S and with COS using typical normal atmospheric concentrations of these gases does not cause formation of Ag_2S tarnishing (reactions 1 and 2) under average atmospheric pressures of these gases, although they do become reactive at pressures a little higher. Although the *standard* free energy change is negative, the *actual* free energy change

is positive at the pressures indicated, indicating that reaction does not take place for the gas pressures considered. This is however true, if and only if, there is no oxygen present. The reason of course, is that if O_2 is present, even at low pressures (> 0.228 mbar according to reaction 13), then oxygen would indeed oxidise the metal to Ag_2O, and this, in turn, can (and does) indeed react with H_2S and COS (reactions 4 and 5). That is important to understand.

2. If the surface is oxidized (by oxygen), and carries an oxide film (Ag_2O), then the Ag_2O film will certainly react with the sulphur gases, H_2S and COS, to produce Ag_2S (tarnish) at their typical normal partial pressures in air (reactions 4 and 5). This would occur at any practical pressure of these reactive gases because the minimum pressure required for reaction is so very low.

3. We note that Table 2 shows that the dissociation pressure of Ag_2O (reaction 13) is 0.228 mbar (the minimum oxygen pressure required to form the oxide), which is far lower than what is experienced from any normal atmosphere (*ca*. 0.2 bar), so Ag_2O is always expected to form on the surface of bared silver. Published work that shows adsorbed oxygen rather than a silver oxide film is thereby unlikely to be correct.

4. The thermodynamic difference between the reactions of Ag and Ag_2O in the description above lies largely in the difficulty of oxidizing the metal in the absence of oxygen. The sulphides, H_2S and COS, are not oxidising agents through their S components, since the S atoms are already in their most reduced form, and they cannot be reduced further. The oxidising agents would therefore be H in H_2S for reaction 1 (which would be reduced to H_2), and C in COS for reaction 2 (which would be reduced to CO). These are however, very weak oxidising agents, far weaker than oxygen itself, and silver is a significantly noble metal. Reactions 1 and 2 can indeed occur, but only if the sulphur gases are at pressures higher than those normally encountered in the environment. Reactions 4 and 5 on the other hand, are not redox reactions, and with the assumption of the prior presence of an oxide film, the oxidation of the Ag atom has already been done. The reactions of the sulphur-containing gases with Ag_2O is then thermodynamically facile. Since oxygen is almost always available in the environment to ensure surface oxidation to Ag_2O, and this can easily react with the sulphur gases, this is the obvious route to tarnishing. The same argument would be rational also for reaction with HCl contaminant in air to produce AgCl.

5. Even in the complete absence of oxygen however, the minimum pressures required to form Ag_2S on metallic Ag (without an Ag_2O surface film) from H_2S or from COS are in fact rather low (reaction 1). In particular, the minimum H_2S pressure (28 nbar) may well be exceeded in industrial atmospheres (15) or in volcanic regions. For example, the partial pressure of H_2S in the geothermally active city of Rotorua (NewZealand) has been recorded at > 50 nbar (16), which is variable, but in excess of the minimum pressure required to form Ag_2S directly from Ag, even without O_2. Detailed study in Thessaloniki (Greece) (15) measured pressures of H_2S hourly of up to 36 nbar. In practice however, such conditions are never without the presence of atmospheric oxygen, and in the presence of atmospheric oxygen, silver sulphide will always form (reaction 4).

6. This raises another important point: we learn from the above discussion, that in *dry* atmosphere, the sulphide of Ag is formed from the oxide, not from the metal itself.

7. Sulphur dioxide (SO_2) in the gas phase is shown to be unreactive with both metallic Ag and with Ag_2O in a *dry* atmosphere (reactions 7 and 8), and cannot produce Ag_2S in the absence of water. This is readily calculated by making simple assumptions about the reasonable concentrations of the partial pressures of SO_2 and SO_3 in air. Reaction 7 is impossible, at any partial pressure of SO_2. Reaction 8 is also impossible at any reasonable pressures of the gases. The notion that SO_2 can disproportionate spontaneously into H_2S and SO_3 in the presence of H_2O is also discounted on thermodynamic grounds.

8. With moisture present however, SO_2 dissolves in water to produce the sulphite ion, SO_3^{2-}, and sulphurous acid, H_2SO_3 (as well as the HSO_3^- ion). These are then reactive towards both Ag and Ag_2O (reactions 3 and 6), and can produce Ag_2S. The reaction thermodynamics for these solution phase reactions are not given because it is not possible to define the relevant concentrations of the solution phases. Notwithstanding this however, calculation of the reaction thermodynamics assuming a wide range of concentrations in solution shows that they would indeed proceed to the right, forming Ag_2S, for any reasonable value of the concentration. Note that reactions 3 and 6 are disproportionation reactions with respect to sulphur, in which the S atom of the H_2SO_3 and SO_3^{2-} respectively, is both oxidized and reduced.

9. Silver chloride (AgCl) forms spontaneously by reaction with chloride, but in the absence of oxygen, it cannot form spontaneously by direct reaction with the metal (reaction 9) when the pressure of HCl is moderate. It can nevertheless form directly from Ag_2O already present on the surface, and indeed, does so (reaction 10). Here, the oxidizing agent is the reduction of O_2. Any chloride in the atmosphere would provide this reaction, irrespective of its origin. In describing AgCl as an origin of tarnish, it should be borne in mind that although HCl and Cl_2 are expected to be of very low concentration in air, chloride can be available in air as a wind-borne salt spray from the sea. Wind-borne salt spray has been shown to be carried inland over remarkably high distances, detectable over many km (17). Now, sea water contains a high concentration of NaCl (0.6 M), which is already aggressive to silver. However, salt spray carried on the wind as water-borne droplets evaporates. That spray also evaporates when it is deposited, and the true sodium chloride concentration in contact with the metal surface from salt spray would be effectively saturated NaCl solution. Often overlooked in marine corrosion problems, the evaporation and associated concentration of salt to saturation level is important. AgCl can be formed from Ag_2S in a marine environment, where the chloride concentration is very high.

10. Important for the understanding of the processes involved in tarnish formation is reactions 11 and 12. These reactions show that if AgCl has formed on the surface, it would in fact react further with H_2S in the atmosphere and be converted to Ag_2S, for all reasonable pressures of the gases involved. It is not necessarily fast, but it is thermodynamically driven. We see immediately now, why surface analysis of tarnish films on silver frequently (but not always) shows the composition to be mainly Ag_2S, with only small amounts of AgCl detected. However, in the presence of moisture, the problem is that of HCl dissolved in water, and that can indeed maintain stability of the AgCl for a normal H_2S gas composition. This observation does not mean that Ag_2S

forms more rapidly than AgCl. It shows simply that Ag_2S is a more stable compound than AgCl, so that any AgCl formed would be converted to Ag_2S over time. This is important for the understanding of the processes. The fact that the natural tarnish on silver is often found to be mainly Ag_2S, with very little AgCl, does *not* mean that AgCl does not form. Neither does it mean that AgCl forms relatively slowly. It means only that if AgCl forms, it will react with any sulphide in the environment to form the Ag_2S, and liberate the chloride ions (reaction 12). It is therefore rational thermodynamically that both AgCl and Ag_2S are found in analysis of tarnish layers, and that the ratio of the two should be very variable. It is worth noting the very tiny pressure of H_2S required to drive reaction 12: essentially reaction 12 proceeds at any partial pressure of H_2S. Reaction 11 on the other hand is expected *not* to occur if the system is moist. This is not contradictory, but shows the clear differences that are expected from different environment compositions. Both Ag_2S and AgCl contribute to tarnish formation.

The conclusion then, is that all three products: Ag_2S, AgCl and Ag_2O, can (and do) form when Ag is exposed to air under average ambient conditions. Ag_2S is generally the most stable, and is the ultimate corrosion product. The tarnishing of silver to form Ag_2S always has a significant driving force, and silver sulphide formation is thereby a thermodynamic inevitability. Any sulphur containing gas in the atmosphere can produce H_2S, although SO_2 is a likely reactant if and only if, moisture is present (reaction 6).

It is noted then, that the sulphur-containing species, gaseous H_2S and COS, as well as the dissolved species H_2SO_3 and SO_3^{2-} are all reactive with Ag_2O, to produce Ag_2S (tarnish). Ag_2O would however, be the first to form on the bare metal in air, by dint of its overridingly high pressure. It is important to realize this. It is also clear that any analysis of the tarnish layer should also contain Ag_2O, in amounts ranging from remnant to significant, depending particularly on the age of exposure, but also critically on the composition of the environment.

Silver as an air purifier

The matter has potential application. On the thermodynamic basis above, silver should be an excellent air purifier for removal of sulphur compounds, including H_2S, COS and SO_2. Particularly the sulphides should be removed to a very low level, as exemplified by the minimum pressure required to cause Ag_2S formation shown in Table 2. The limitation to this process would be the kinetics, and not the thermodynamics. Indeed, since the process of forming Ag_2S should be *electrochemically* reversible, such an air-purifying system would be “rechargeable”. Most silver compounds are electrochemically reversible: hence the widespread use of silver as a reference electrode (particularly AgCl/Ag) in electrochemistry.

Many more possible reactions can be written, some of which are thermodynamically possible and some of which are not. We consider here reactions with metallic Ag directly, and also, reaction with the oxide, Ag_2O. This is important because one would normally consider the metal already to be covered with an oxide film before tarnishing commences. Tarnishing is necessarily a slow process because of the low (or very low) partial pressures of the tarnishing reactants in normal air. However, with the metal in an open atmosphere, continuous passage of air would allow reaction with sulphur-containing vapours, even at very low concentration. The matter of whether the tarnishing components of the atmosphere can already be incorporated during formation of the first oxide layers, is nevertheless important, and is approached below.

Closed and open systems

It is worthwhile mentioning here, that because of the low partial pressures of sulphur-containing and chloride-containing components of the atmosphere, it follows that closed systems are favourable for avoiding the formation of tarnish. In relatively small volume, there would simply be insufficient S-carrying gas to create a visible tarnish, and once reacted, the S-carrying gas would be then at negligible pressure. Indeed, because silver is so very sensitive to reaction with sulphide, a sealed container for items to be protected could well be equipped with a vessel containing a quantity of high-surface-area silver (such as microparticulate silver with a high specific area) to act as an effective “getter” for the corrosive sulphur-containing (and chloride-containing) gases. It is an interesting issue because of reactions 4 and 5: because of the extremely low minimum pressures of S-containing gases which are required for reactions 4 and 5, the oxide film in a truly closed system should remove effectively all of the S-containing gases. It would provide a method of providing S-free environments (but only in a closed system).

The basic mechanism of tarnishing of silver in air

Silver tarnishes because the normal oxide film (Ag_2O), which is expected to form very rapidly on the surface of the metal as soon as the bare metal surface is exposed to air, is converted to Ag_2S by reaction with sulphur gases, particularly H_2S and COS (as well as to AgCl by reaction with atmospherically borne chloride). The prime reason for formation of the tarnish is the very high stability of silver sulphide, relative to the stability of the oxide. The relative stability of the two compounds is quantified by comparing the standard chemical potentials Table 1, and the free energies of reaction Table 2. Second, Ag_2S also has extremely low solubility in water (3.4×10^{-16} M at 25 °C), far lower than that of the Ag_2O (5.6×10^{-5} M) (at 20 °C) (12). Even the chloride (AgCl), whilst considered insoluble in water, is in fact far more soluble than the sulphide (12). Both these facts: the stability of the sulphide relative to that of the oxide, and its relative insolubility, are fundamental to tarnishing of the metal. The issue of solubility is very important in moist environments.

Although all the gaseous sulphur-containing compounds in the natural environment normally have a low (or very low) partial pressure, the high stability of Ag_2S, and its extremely low solubility in water drives tarnish formation on the surface. A very low partial pressure of the sulphur gases means that on exposure to the atmosphere, it is almost always silver oxide that would form first when a freshly-bared silver surface is exposed. The oxidising agent is atmospheric oxygen to form Ag_2O, which then reacts. However, the sulphide is much more stable than the oxide in any of the sulphur-containing gases normally encountered, and so the conversion of Ag_2O to Ag_2S should be regarded as inevitable, albeit slow. It is the relatively fast kinetics of the reactions to form Ag_2O that makes the oxide form first on a freshly bared silver surface, chiefly because oxygen and water vapour are so abundant in air. It is however, the thermodynamics of the sulphide that enforces eventual formation of silver sulphide from the already-formed oxide (and thereby from the metal): that is tarnishing.

Oxidation in dry air

To take the discussion further, we must consider the differences between reaction in *dry* air, or air of low moisture, and the reaction in *moist* air. In both cases, the surface is covered initially with the oxide, with negligible contamination of sulphide. The reason for this is the fact that the oxygen content of air is overwhelmingly high in comparison with the normal sulphur- and chlorine-containing gas content, typically 10^9 to 10^{10} times the tarnishing-gas content (see Table 2). Now, assuming the contaminant gas is H_2S or COS (for sulphur) (and HCl for chloride), the contaminant atom is already in its most reduced form, and cannot be reduced further – so it cannot be the oxidizing agent. The reduction of oxygen is therefore the required oxidizing agent, and that cathodic reaction must take place on the silver surface where the metal atom is being oxidized.

We consider first the case of dry (or nearly dry) air. The basic formation of Ag_2O from silver in air can be written as:

$$Ag \rightarrow Ag^+(f) + e^- \qquad (14)$$

and

$$O_2 + 4e^- \rightarrow 2O^{2-}(f) \qquad (15)$$

where (f) denotes the ion in the oxide film. Equation 14 is the oxidation of the metal and 15 the reduction of oxygen. We separate these two reactions deliberately. In the first instance, oxygen must come into direct physical contact with the metal, so that electron transfer from Ag to O_2 can occur. At that stage, before the first monolayer of oxide is complete, this is a simple chemical reaction, involving collision of the two reactants. However, once the first monolayer (or more) of Ag_2O is formed, the metal and the oxygen can no longer come into contact with each other, but the process must occur if the oxide film is to thicken. (Note that 1 oxygen molecule oxidises 4 silver atoms.) To do this we must understand how these two reactants can react without actually meeting each other.

The oxide ions required to form Ag_2O are therefore already in situ. At such low pressures of contaminant gas, the probability of the contaminant gas (such as H_2S, COS, or HCl) being in the vicinity, and close enough to allow its reaction must be vanishingly small, so the oxide must be formed first, without sulphide or chloride. This means that the initial surface oxide cannot contain and significant quantity of S^{2-} or Cl^-. (Note that for chloride formation in marine spray environment containing NaCl, there is very much chloride present, and the argument therefore fails – we discuss the wet system below.)

Some further comments are important too. The initial reaction is reaction 13 (the same as reactions 14 and 15 together), but it does not necessarily require formation of three-dimensional crystals of Ag_2O. Indeed, the earliest stages of oxidation cannot involve crystal formation. Such a reaction can be so fast, that the first atomic layer is simply a two-dimensional array of Ag^+ and O^{2-} ions bonded randomly across the surface into a network. This has been proposed in the early stages of electrochemical oxidation (in water, see below) (18,19), and is likely to apply here too.

Crystallization of the surface oxide of such an oxide requires formation of a three-dimensional array, and must be a much slower process.

If we imagine now, that the first monolayer of oxide has been laid down very quickly, then thickening of that oxide film beyond the first monolayer ensues. However, now the metal atom to be oxidized (reaction 14) is separated spatially from the oxidizing O_2 gas (reaction 15), and they cannot meet, at least prior to reaction. The separation is that of the thickness of the already-formed oxide. That separation would be only one molecular layer thickness immediately after the first monolayer has formed, but increases as the already-formed layer thickens. The process requires that the oxygen molecule in the gas phase can *sense* the presence of the metal atom, and that the metal atom can sense the oxygen, but it is impossible for the two reactants to make direct contact. It is an interesting reaction: once the first full monolayer of oxide has been formed, the reaction of these two chemicals (Ag and O_2) occurs without their actual intermolecular (or interatomic) collision. This (apparently) odd behaviour is fundamental to almost all metal corrosion and oxidation processes. Normally, reaction between two chemicals requires collision between the reacting species, in the absence of which, no reaction can occur. So that now raises the question, as to how one of the reacting species (Ag or O_2) can recognise the presence of the other one, and vice versa in the absence of direct contact of the reactants.

The answer lies in the fact that this reaction is an *electron transfer* process, with the electrons of the Ag atom being passed to the oxygen molecule – basically an electrochemical process. That is special. Movement of electrons constitutes (and indeed defines) an electric current, and as with all electric current flow, is driven by a voltage. Thus, we deduce that there is inherently an electric field across the existing film that drives this electron current, and thereby the reaction. It is the electric field that allows the reactants to recognize each other. Ag_2O is of course, electronically conducting. Because these are redox reactions, requiring the transfer of electrons from the metal atom to the oxygen molecule, and electrons a driven by an electric field, it is this field that creates the reaction.

Now, passing electrons across from the Ag to the O_2 means that at any instant during oxide film growth, there is inherently a surplus of Ag^+ ions at the metal/oxide interface, and a surplus of O^{2-} ions at the oxide/gas interface, because the electrons are driven across by the electric field, but at that stage, nothing further has happened. The interfacial excesses of Ag^+ and O^{2-} are now the driving force for *diffusion* of one (or perhaps both) ions across the existing film. Which ion diffuses across the existing oxide for it to grow further depends largely on the nature of the defects in the existing Ag_2O, and its relation to the structure of theAg_2O film. As the oxide film thickens, so the rate of further oxidation declines, because the mass transport of ions across the film is much slower than the electron transfer (and the electric field decays). Since it is a concentration gradient across the film that drives the diffusion of the ions, then the rate of oxide growth decays because the concentration gradient declines as the film thickens. Oxide films form on very many metals in this manner in dry air (and in moist air too) at ambient temperatures, and they are very thin: silver oxide is no exception. Silver can thereby maintain a bright metallic lustre for very long periods of time provided the environmental components are benign to the stability of its oxide.

In describing this mechanism, we note some features which should be understood. When an oxygen atom is reduced to O^{2-} at the film/environment surface, then inherently, the oxide surface carries two Ag^+ ion vacancies, because no Ag^+ ion has yet been transported: diffusion of ions is much slower than conduction of electrons. We can therefore describe the reactions as vacancy diffusion under a concentration gradient of ion vacancies. It should also be understood that the transport of electronic charge across the oxide film means that both interfaces of the oxide are charged electronically, as a capacitor, but it is a leaky capacitor.

This means now, that the much slower formation of the sulphide/chloride tarnish occurring from air containing the S or Cl contaminants, takes place by transformation of the already-existing oxide film. The rate depends on the partial pressure of the contaminant gas, and it is slow because the ambient partial pressures of these gases are generally low or very low. These can typically be around 1 nbar. The contaminant gas reacts first with the outermost layers of the oxide, basically by replacement of the oxide ions in the surface of the oxide with S^{2-} (or Cl^-). The reaction can be written

$$O^{2-}(f) + H_2S(g) \rightarrow S^{2-}(f) + H_2O(g) \qquad (16)$$

where (f) and (g) represent film and gas phases respectively. This is reaction 4, rewritten to emphasize the role of the ionic reactants, and the fact that ionic excesses, and corresponding ion vacancies occur at the interfaces.

Now, the molar volumes of Ag_2S and Ag_2O (crystalline) are very similar: per mole of Ag atoms, these are 16.91 cm^3/mol and 16.22 cm^3/mol respectively (13)), with the sulphide having the slightly bigger volume, so this substitution of sulphide ions for oxide ions cannot be a difficult one. Further transformation beyond the first first layer requires diffusion in the silver oxide film itself, and this must be slow: however it is likely nevertheless, to be facilitated by the slightly greater molar volume of the sulphide. This greater molar volume arises because the sulphide ion is larger than the oxide ion, and its presence in the oxide lattice would cause a greater defect density within that lattice, facilitating diffusion within the lattice. If the defect density is sufficiently great, this may lead to cracking of the oxide film, which would enhance the tarnishing process. The transformation may also be facilitated by the fact that both Ag_2O and the α form of Ag_2S have cubic structure. It is in fact likely that the transformation to the monoclinic β form of Ag_2S (acanthite) may occur subsequently, as a result of the lattice strains induced by reaction.

We note here in passing, that Ag metal has a molar volume of 10.27 cm^3/mol (13), significantly smaller that the oxide. So forming the oxide from the metal would involve creating compressive stresses in the thin film as it grows. Converting that oxide film subsequently to the sulphide would increase those stresses from the outside surface, and may well cause cracking and buckling. Again, any buckling of the films would facilitate tarnishing.

It is likely that these transformations involve crystallisation of the initially formed amorphous oxide film, and that crystallization would itself accelerate the oxidation process significantly. An increase the overall film thickness would occur, because the crystallisation would create grain boundaries, and perhaps other intercrystalline regions, which would rapidly form more oxide. Tarnishing to form Ag_2S or AgCl thereby involves formation of a film significantly thicker than the original oxide film.

In summary, the tarnish occurs very much more slowly than growth of the oxide, by reaction of the contaminant gas with the oxide itself, converting Ag_2O to Ag_2S or AgCl (or both), generally with Ag_2S being the most stable in air. Note that in transforming silver oxide to the more stable silver sulphide or silver chloride more defects in the oxide film system are created, pareticularly in the tarnish crystals, in the intercrystalline regions, in the grain boundaries, and in the now heterogeneous composition of the surface film. All these enhance corrosion, causing further tarnish formation and film thickening. However, it appears that growth of the tarnish layer also slows down as the sulphide thickens, retarding by preventing access of the atmospheric oxygen to the metal surface.

The role of water

In dry air, the reactions of silver to produce tarnish are known to be very much slower than the same systems in the presence of moisture. The reasons for this are several fold, and are fundamental to all metal corrosion reactions in aqueous environments. Metal corrosion reactions are redox reactions, in which the metal is oxidized and a component of the environment is reduced. So the basic differences in the presence of moisture are as follows.

1. In a *dry* system, there is no electrolyte, and the oxidation and reduction reactions lie directly over each other. If there is an intervening oxide film, as is necessary in dry air, then the oxidation and reduction reactions are spatially separated by approximately the thickness of that oxide film alone, and transport of electrons and ions takes the shortest path, which is directly across the existing film. They cannot be spatially separated across the surface because there is no electrolyte.

The presence of *moisture* allows the separation of the oxidation and reduction reactions laterally across the surface, and this separation can be very wide. This is made possible, because water functions as an electrolyte (ie an ion conductor). It may sound trivial, but it is not. It means that the cathodic reduction of the environment component does not have to occur directly over the oxidizing metal atom, so each cathodically reactive molecule (such as atmospheric O_2) can oxidise any silver atom, even quite remote from its own position. Depending on exactly how conductive the electrolyte is, the separation can be enormous. This process changes the mechanism of corrosion, and it also accelerates the reaction enormously: both the corrosion and the passivation reactions are accelerated in this way.

2. The presence of moisture provides alternative reduction products, and oxidation reaction products from the metal. This is seen already in some of the reactions above, where reactions of SO_2 to produce tarnish are shown to be thermodynamically difficult in the absence of water, but thermodynamically facile in the presence of water. Now, the reduction of oxygen (the cathodic reaction) produces H_2O or OH^-, as

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad (17)$$

or

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (18)

and the consumption of ions (H^+) or creation of ions (OH^-) causes ion conduction in the electrolyte, changing the chemistry locally over the surface.

3. We note here, an important and fundamental process in aqueous corrosion reactions: the cathodic site on the surface becomes more alkaline (reactions 17 and 18). Correspondingly, the site of the anodic reaction (oxidation of Ag) becomes more acidic. Silver is more aggressively attacked in acidic solution, so the anodic sites can attacked faster. The cathodic sites are correspondingly more passivated because silver is more passive in more alkaline solution.

4. The presence of moisture provides a pathway for *dissolution* of the oxidised Ag. (Dissolution cannot occur in dry gas-phase corrosion.) The dissolved Ag^+ allows formation of other reaction products, or perhaps, the same products via a different mechanism.

5 . The presence of moisture also allows other components of the environment to be dissolved, raising the possibility of a number of other corrosive reactions. For example, some wood species emit acidic vapours, such as formic acid or acetic acid very slowly over time (23-27). These vapours, which dissolve in moisture, are corrosive to Ag (as well as many other metals, including Cu and Zn), by enhancing dissolution of the metal as Ag^+. Such dissolution is caused by the acidification of the moisture in contact with the metal, as well as the fact that the solubility of the Ag salts (silver formate or acetate) have significant solubility in water. Any protective film of Ag_2O is thereby attacked by these acidic solutions. Formation of silver compounds in solution is then accompanied by precipitation when the surface moisture becomes saturated or simply evaporates. Aggressive vapours emanating from wood accelerate the formation of tarnish on silver, by allowing more silver to dissolve. The matter can be a problem when storing silver in wooden cabinets, and is discussed below. Water is also a solvent for H_2S and for HCl etc.

All the above points explain the fact that at a given temperature, corrosion of silver in a humid environment is accelerated greatly by the presence of moisture, relative to the corresponding process in a dry environment. The process of tarnishing is also this accelerated by moisture.

Electrochemical processes leading to tarnishing.

As with all metal corrosion processes, the oxidation of the metal requires an oxidizing agent in the environment. For the noble metals, including silver, this is normally oxygen from the atmosphere, which is reduced to water (or oxide ions). Unlike the base metals, such as iron, aluminium and titanium, the reduction of water to hydrogen does not normally cause oxidation of silver. The matter is not quite so clear-cut however. By combination with sulphide or with chloride, the metal is rendered much less noble than it is in the absence of these environmental components: this is the consequence of the high thermodynamic stability of Ag_2S and AgCl relative to Ag_2O. The anodic (oxidation) reactions of the metal are thereby:

$Ag \rightarrow Ag^+ + e^-$ (19)

$Ag + Cl^- \rightarrow AgCl + e^-$ (20)

$2Ag + S^{2-} \rightarrow Ag_2S + 2e^-$ (21)

The standard electrode potentials for these reactions are respectively +0.799 V(SHE), +0.22233 V(SHE) and -0.679 V(SHE).

We note here, that the reaction with H_2S (rather than with S^{2-}), as:

$2Ag + H_2S \rightarrow Ag_2S + 2H^+ + 2e^-$ (22)

has the much higher standard electrode potential of -0.0366 V(SHE).

This renders silver sulphide a thermodynamically more stable compound than silver chloride, at least under *standard* conditions (but the actual relative stability depends also on the relative concentrations of sulphide and of chloride). The effect of this is that if AgCl were to be formed in the first instance, then it could convert to Ag_2S if sufficient sulphide ions or H_2S were present. It also accounts for the sometimes-reported observations (5) that the composition of the tarnish on silver comprises mainly the sulphide.

We should note here, that if silver is considered in a sulphide environment, it should be regarded as a “base” metal, since its standard electrode potential via reaction 21 lies far below the hydrogen *equilibrium* potential, even in neutral environment (-0.414 V(SHE)). Of course, it becomes more difficult to form Ag_2S as the sulphide concentration in the environment is decreased. However, even at a sulphide concentration of 1 nM in neutral water (which is very low), the equilibrium potential for reaction 21 (-0.425 V(SHE)) lies below that of the hydrogen reaction in neutral water, and we deduce that this low concentration of S^{2-} in water could react with Ag (and any oxide already present), even in the absence of oxygen, to cause slow depassivation and tarnish.

In assessing the formation of tarnish on silver, a further major factor must be realized: the solubility of Ag_2S in water is very low indeed. The solubilities of relevant Ag compounds are listed in Table 3. A consequence of that low solubility is the very low concentration of S^{2-} in the aqueous phase, or low pressures of H_2S in the gas phase that are required to precipitate the sulphide on the metal surface. That low solubility means that any silver which dissolves into the moisture condensed on the surface is precipitated as Ag_2S by trace amounts of sulphide in solution. In fact, both Ag_2S and AgCl have low solubility in water, but that of Ag_2S is far lower, as listed in Table 3.

Compound	Temperature. °C	Solubility per formula. M, or mol/L	Solubility per mole of Ag. M, or mol/L
Ag_2O	20	5.6×10^{-5}	1.1×10^{-4}
Ag_2S	25	3.4×10^{-16}	6.8×10^{-16}
AgCl	10	6.2×10^{-6}	6.2×10^{-6}

Table 3.
Solubility of Ag_2O, Ag_2S and AgCl in otherwise pure water at ambient temperature. Data from reference (13).

The dissolved silver cation (Ag^+) reacts with chloride and sulphide from the environment to give:

$Ag^+ + Cl^- \rightarrow AgCl$ (23)
$2Ag^+ + S^{2-} \rightarrow Ag_2S$ (24)

In a moist environment, the Cl^- and the S^{2-} in the environment lie in the thin film of moisture that overlies the metal surface, or perhaps from air-borne nanoparticulate matter, or from some gas components within the air dissolved in the moisture. (Gas phase reactants cannot be ionic, but may ionize when dissolved in water.)

The problem with tarnishing by these reactions lies in the fact that none of the reactions with sulphide or chloride causes true passivation of the metal, although the progress of these reactions does reduce the further rate of tarnishing. Only the oxide film, formed by reaction with water, can cause true passivation (see below). It is therefore important to examine and understand what causes passivation of metals, not only silver, and what differences there are between passivation and continuing corrosion.

Passivation of silver in aqueous environment

Passivation of a metal involves the formation of a solid surface film, usually the oxide, which separates it from the environment. The surface film which engenders passivity is usually the oxide formed naturally by reaction with the environment. The state of passivity of a metal is remarkable, truly remarkable. Metals which passivate do so by mechanisms which allow the oxide film to cover the surface completely, with no gaps, and no exposed metal atoms: essentially a passivating blanket. If gaps do develop, such as during abrasion, or perhaps by cracking under deformation, the passive metal surface recovers by *repassivating* to form the same protective oxide again. With no gaps, any further oxidation of the metal which takes place (and it does indeed take place) forces the oxidizing metal atoms into the already existing oxide film, and not into the environment. The consequence is that the oxide film thickens. The process can lead to extremely slow oxidation rates. Although corrosion still occurs in the passive state (because the metal is still thermodynamically unstable), its rate is inherently slow, and can be extremely slow. (see eg. 28)

One can view the mechanism of passivation from the stepwise mechanism of the anodic oxidation of the metal atom from the surface. The mechanisms proposed below are based on studies of the passivity and corrosion of many metals, including, but not restricted to silver. We note immediately, that most metals in service are already in their passive states, and covered with a protective oxide film. With the exception of gold, metals already carry their oxide film when in contact with air. To study passivation of metals, it is necessary to generate first a bare metal surface, and this process can be more difficult that it may first appear. However, if we imagine the metal to be bare, in the first instance, then the following describes the basic steps of passivation.

Formation of the first oxidized monolayer in aqueous solution.

It is important to understand whether the aggressive ions, such as sulphide and chloride, enter into the first steps of passivation (or corrosion) when the metal is first exposed to the wet system. Fortunately, in the wet system, it is possible to apply electrochemical methods to this problem, which means they can be examined unambiguously *in situ*. In electrochemical methodology, the electrochemical reaction can be controlled and measured, because of the electron transfer, and the electrolyte involved.

In the case of the general metal, the first step is the adsorption of water to the surface: in water, in moist systems, or in humid atmosphere, adsorption of water is easy. For silver from its bare surface:

$$Ag + H_2O \rightarrow Ag(H_2O)_{ads} \qquad (25)$$

The first electron transfer step then forms the first reaction intermediate adsorbed to the surface, as

$$Ag(H_2O)_{ads} \rightarrow AgOH_{ads} + H^+ + e^- \qquad (26)$$

This step has been established by many techniques. One in particular uses a diamond stylus to scratch the surface of the metal under immersion in aqueous solution *in situ*, while simultaneously following the fast electrochemical reactions that ensue: this reaction is very fast when the metal is in contact with water (18-22). The technique ensures unambiguously that the new surface is initially completely bared metal, with no prior covering, and that its first reaction is then with the environment under study. Detailed description of this method is available in the published literature (18-22). What happens to the adsorbed AgOH intermediate beyond the reaction above now determines whether the metal passivates or dissolves.

We note at this stage, that the bulk compound of stoichiometry AgOH (silver hydroxide) is not known to exist although Pourbaix (13, p. 393 *et seq*) mentions such a compound, termed “hydrated silver oxide” as being highly soluble in water. Pourbaix gives an extremely high solubility for AgOH (13). However, this does not preclude its formation as a stable *monolayer* compound, essentially two-dimensional, adsorbed to the metal surface. Nor does it preclude its formation as an adsorbed intermediate during the further reaction of the metal in aqueous solution. Its stabilisation energy in that form comes from its adsorption energy, and its structure at that interface.

Passivation from the first oxidized monolayer

In order to passivate silver, it is necessary to form the passivating oxide by reacting this adsorbed intermediate to produce an oxide film directly on the surface via either of the following:

$$AgOH_{ads} + Ag \rightarrow Ag_2O + H^+ + e^- \qquad (27)$$

Reactions 26 and 27 do *not* involve the formation of a dissolved Ag^+ ion: this is an important feature of the mechanism of passivation. The entire reaction takes place on the surface of the metal, without dissolution of the Ag^+ ion. This is a crucial part of the understanding of passivation and passivity of the metal: the passivating oxide forms directly on the surface of the metal, without the metal cation first entering the solution phase. For the Ag component of the oxide, it is a solid-state reaction only. Notice that reaction 27 involves the intermediate AgOH *losing* its H^+.

Dissolution from the first oxidized monolayer

If the surface intermediate (AgOH) *does* form the dissolved ion, then the metal corrodes, as:

$$AgOH_{ads} + H^+ \rightarrow Ag^+ + H_2O \qquad (28)$$

and the metal ion is thereby dissolved. It is easy to see (but nevertheless subtle) that the real difference between reaction 27 (passivation) and reaction 28 (dissolution) lies in the behavior of the hydroxide component of the AgOH. If that hydroxide component *loses* the proton (reaction 27), the oxide (Ag_2O) forms *without* first dissolving as Ag^+, and the metal passivates. If that hydroxide component *gains* a proton, (reaction 28) then water is formed from adsorbed AgOH, and the silver component dissolves as Ag^+. Bearing in mind that movement of H^+ in an aqueous system is extremely facile (the most mobile ion in water), the balance between these two reactions is subtle, and very pH-sensitive. Note again, that the Ag atoms which cause passivation by oxide formation do not enter the water phase as dissolved ions at all, but remain on the surface throughout the reaction and that this reaction involves the AgOH intermediate *gaining* H^+.

It is now important to realize that, by contrast to the passivation process (reaction 27), the dissolved Ag^+ cation may indeed precipitate out on the surface as a solid oxide, with

$$2Ag^+ + H_2O \rightarrow Ag_2O + 2H^+ \qquad (29)$$

This oxide is also Ag_2O, but by reaction 29, it is now formed by a *dissolution-precipitation* mechanism, where the oxide is deposited from solution, and cannot of itself be passivating. The reason that this cannot be passivating is that in order to form an oxide by dissolution followed by precipitation, it is necessary to form crystals of Ag_2O from the dissolved Ag^+: without this, no solid phase can be formed at all. The crystals are inherently 3-dimensional and they already have shape when they deposit on the surface. They cannot therefore cover the surface completely, even when there is a fairly heavy deposit because they must always leave gaps between the crystals, and where they meet the surface. As a consequence, there are always gaps in oxides formed by dissolution-precipitation, and the remaining exposed metal atoms in the interstitial regions can dissolve, leading to corrosion. That is a fundamental difference between the oxide formed by reaction 29 and that formed by reaction 27. It is also a fundamental process by which passivation (by oxide formation) lies in contrast to the process of corrosion product formation (also oxide formation): the former is a surface solid-state reaction (or more correctly, and adsorbed-state reaction), whilst the latter is a dissolution-precipitation reaction from solution.

This basic mechanism is common to many metals. For example, when iron (or steel) is exposed to a passivating solution, such as an alkaline borate solution (pH 9), an invisible oxide film of iron oxide is formed, which is very thin, and which passivates the metal. The metal can remain passivated that way for a very long time. If however, the same iron is exposed to acidic solution, the metal dissolves (as Fe^{2+}), and will do so continuously. Some of the dissolved metal ions nevertheless precipitate onto the surface as a thick oxide deposit (rust): the rust layer does *not* passivate the metal, for the same reasons that reaction 29 does not passivate silver, and the metal continues to corrode.

The next question is: does the aggressive ion enter these first steps of passivation and dissolution of silver, and how can that be detected. Chloride is considered here.

Transient electrochemical reactions of the scratched silver electrode in solution
We can detect these first step by analyzing the current transients that are found when silver is scratched transiently under immersion in solution, whilst held under control of the electrode potential (potentiostatically). Full details are reported in references 18,19,29,30. We show such a current transient in Figure 1: the current is anodic throughout. The current shown has been rescaled so that it represents only the scratch current, and it is shown starting at the time the diamond stylus first makes contact with the metal (t = 0). In these experiments, the diamond stylus is driven onto the rotating metal surface, and then withdrawn after a brief contact period. Whilst the scratch is being created, the current rises continuously and linearly with time. When the stylus is withdrawn from the surface, after 0.4 ms from first contact, the current decays continuously and immediately. This rise in anodic current is the oxidation of the metal. The fact that the current decays continuously is passivation.

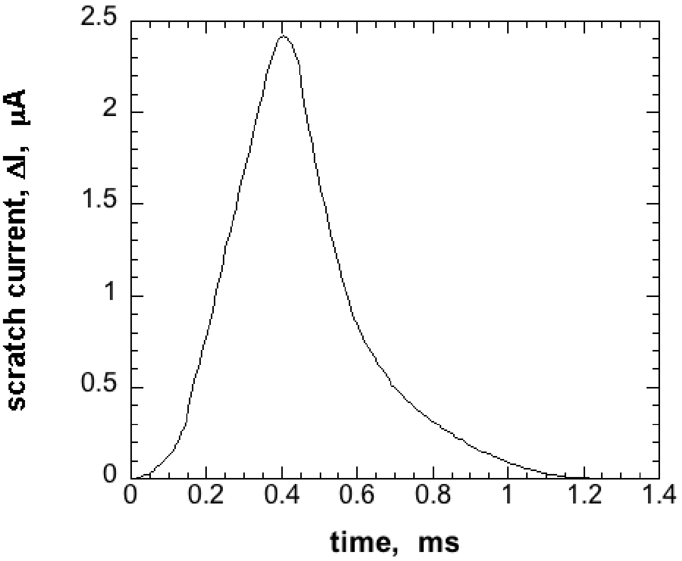

Figure 1
Anodic current transient generated by scratching Ag in 0.1M HCl/0.9M $HClO_4$, pH = 0 at a potential of -141 mV(SHE). The current and time axes have been rescaled to 0 at the point that the scratch commences. The scratch duration is 0.4 ms. Data from ref. 30.

Now, we can integrate the current with respect to time, to show the charge passed, which is directly related to the amount of oxidation that has occurred on the scratch surface. This is important, because it shows much information. Figure 2 shows the same current transient as Figure 1, but now also shows the integrated charge on the same plot: both the scratch current, and the charge passed on the scratch, are thereby shown as a function of time. Note that the currents are very small, measured in μA (and less), and the charges are also tiny, measured in hundreds of pC (and less). These numbers are tiny because the scratches are tiny, and when normalized to the surface area of the scratch, are much more significant.

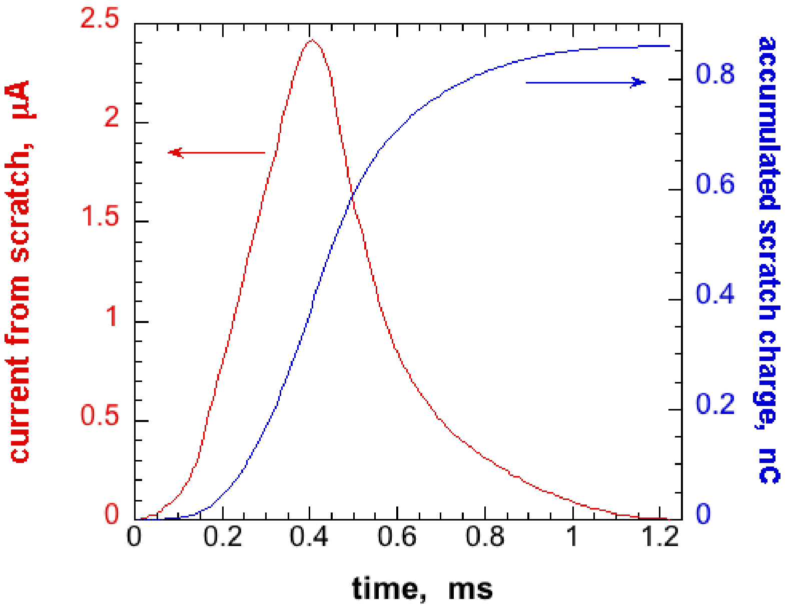

Figure 2
The same scratch current transient as Figure 1, but showing now the corresponding integrated charge. Data from ref. 30.

Now, to understand these results, it is necessary to plot the current decay as a function of the charge passed, since it is the passage of scratch charge that causes the scratch current to decay. We show some plots of this in Figures 3 and 4: these graphs show the data now normalised to the surface area of the scratches involved to give the scratch current *density* and the scratch charge *density*.

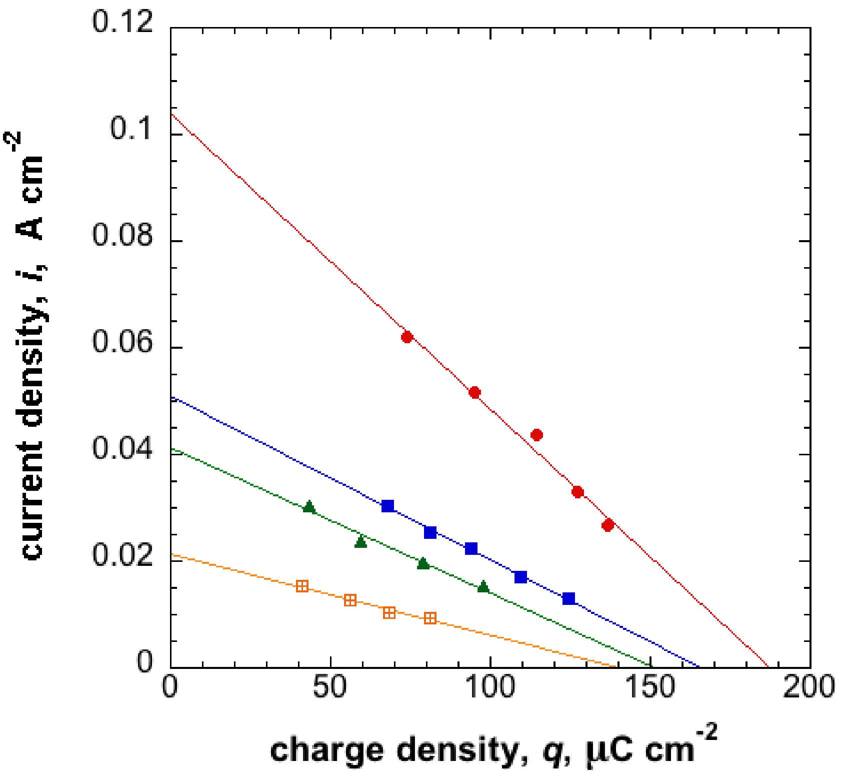

Figure 3
The current density flowing from scratches on silver in 0.1M HCl/0.9M $HClO_4$, pH = 0, as a function of the charge density passed. In ascending order of current density the potentials in mV(SHE) are: -266, -191, -141, -66. Data from ref. 30.

Figure 3 shows this relationship for a mixture of 0.1M HCl with 0.9M $HClO_4$, pH = 0. The plots for all three potentials show that the current density decays linearly with increase in charge density passed. We see the same linear relationship in Figure 4, for 1.0M HCl, (ie 10 times the chloride concentration of Figure 3), also of pH = 0, but the current density is higher.

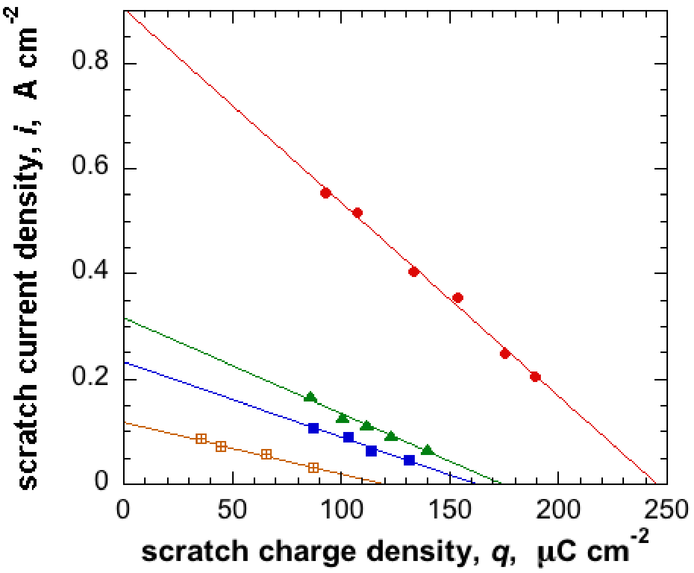

Figure 4
The same as in Figure 3, but this time in 1M HCl, pH = 0. The potentials are the same as in Figure 3. Data from ref. 30.

Much is learned from this. First, the linear decay in current with increase in charge means that the surface film being formed is effectively blocking this fast reaction. As the coverage of this film spreads over the surface, so the anodic reaction continues only at that part of the surface not yet covered by the oxide. It is a very simple formation of the network of the first layer of the passivating film. Second, the presence of higher concentration of chloride accelerates the reaction (higher current density for any given charge density). So, chloride *must* enter that first step of the reaction, and *must* form part of the oxidised monolayer. Third, the reaction is accelerated by raising the potential as well: this is expected from classical electrochemical kinetics. Fourth, since the current density decays linearly with the charge density passed, we can legitimately extrapolate the graphs to the axes. This produces the current density on the truly bare surface, before any reaction has occurred ($q = 0$) as well as the charge density required to passivate the surface fully (ie when $i = 0$). We call this charge density when i is extrapolated to 0, the "monolayer charge density".

Figure 5 shows now, a plot of the monolayer charge density against potential. The graph displays two regions of potential which show plateau charge densities for this. The first shows a mean charge density of *ca*. 240 µC cm^{-2}: this value is approximately what would be expected from oxidizing half of a monolayer of Ag atoms. The second plateau in charge density is *ca*. 420 µC cm^{-2}, and lies at slightly higher potential. This represents approximately one full monolayer of oxidized metal atoms. These assignations arise because part of the monolayers must be occupied by OH^- or O^{2-} anion to provide the completed monolayer. The two charge density plateaux are representative of the two different monolayers of the first oxide formed on the surface: the lower value is the AgOH layer, and the higher one, the Ag_2O layer. Since

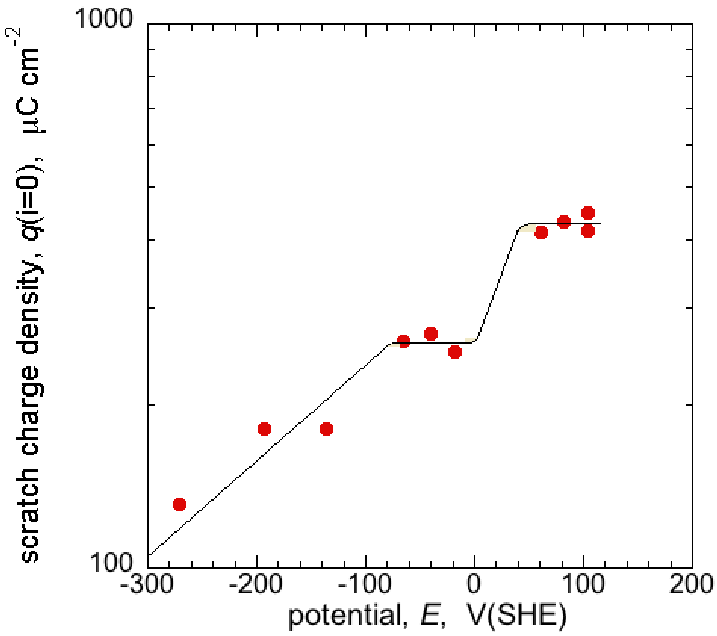

Figure 5
The scratch charge density extrapolated from the linear current density/charge density plots to zero current, as a function of potential. This is the monolayer charge density. The data were measured in 1M HCl, pH = 0. Note the two plateau in charge density. Data from ref. 30.

the chloride accelerates the reaction in *both* regions, we deduce now, that the Cl^- anion enters both these first oxides as they form. We note that the potential ranges covered by these experiments are below those at which bulk silver oxide can form (13), and below those at which Ag can anodically dissolve at a significant rate (13).

It is also instructive to show the monolayer charge density as a function of the Cl^- concentration in solution, plotted now, in Figure 6 for constant potential. The lower plateau charge density is independent of chloride concentration, which is probably not surprising because Cl^- and OH^- are approximately the same diameter, and adding Cl^- into the monolayer would not change the amount of Ag oxidized – that is to say, a two-dimensional monolayer of AgOH and of AgCl (and a single monolayer containing both anions)) would show approximately the same amount of oxidation, and therefore the same monolayer charge density. However, the higher charge density region is dependent on the Cl^- concentration, and we deduce thereby that the presence of Cl^- in the Ag_2O layer does indeed increase the amount of metal oxidized, probably by disrupting the structure of that oxide. The experiments are thereby unique in providing insight into the earliest stages of silver oxide formation.

Unfortunately, there are no similar data available for reaction of the bared surface with aqueous sulphide.

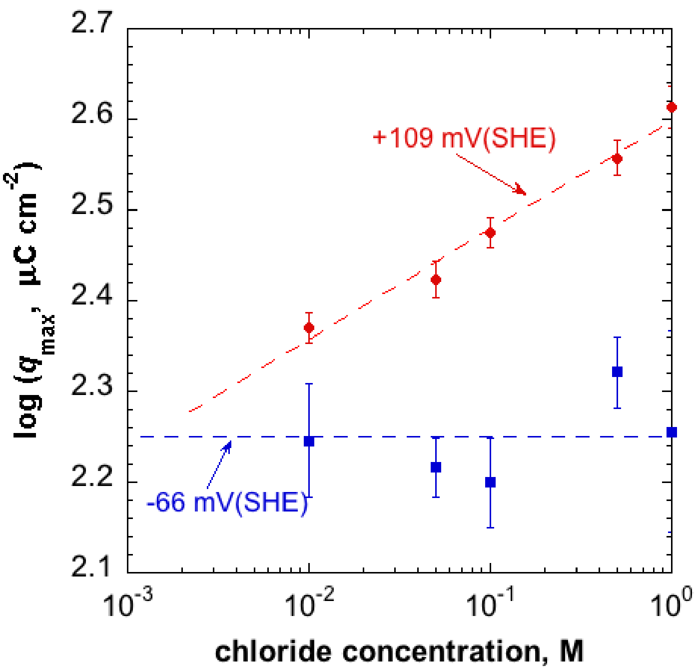

Figure 6
The plateau charge density from scratched silver measured as a function of the chloride concentration. This is the monolayer charge density for the two plateau regions as shown in Figure 5. Lower charge density (squares) measured at -66 mV(SHE). Upper charge density (circles) measured at +109 mV(SHE). Error bars show the standard deviation of multiple measurements. Data from ref. 30.

However, we can deduce from these experiments that the aggressive ions do indeed take part in the earliest stages of reactions of the bare surface, if the surface is really bared. Although it is expected that the initial surface carries an oxide film, we can rationalize that any part of the surface that becomes bared would react with Cl^- provided there was sufficient Cl^- in the environment to cause that to happen. Such a case could be in the presence of salt spray, or evaporated salt spray. In atmospheric tarnishing, the sulphide ion (or H_2S) is unlikely to be present to sufficient concentration for that to happen at a significant rate.

Further aspects for tarnishing of silver

Silver has a rather unique property of forming insoluble (or sparingly soluble) compounds with a great many anions. This is fairly unique and for silver has a great influence on its tarnishing characteristics for the following reasons.

First, when silver oxidises to form a compound, the sparing solubility of the compound causes the solid salt to precipitate dissolved Ag^+ from solution onto the metal surface: this inherently deposits in microparticulate or nanoparticulate form. That deposited solid salt is not passivating: it cannot be because it cannot cover the surface completely. Particles deposited from solution phase cannot tessellate over the surface, and there must always be gaps, between the crystals as well as underneath, where the crystal is not flat on the surface. There is thereby always room for active corrosion, if the metal can dissolve in that environment. Note however, that the deposit can indeed reduce the rate of corrosion, and significantly so, by retarding movement of ions and of water molecules through the interstices to the metal surface. This is not a true state of passivity.

Second, is the fact that many silver salts are more stable than the metal oxide (Ag_2O). This presents a real problem, because although it is expected that the oxide should passivate the metal, it is also reactive towards conversion to insoluble salts. Most notably, these are the chloride, AgCl, and the sulphide, Ag_2S, both more stable than the oxide, and both more insoluble in water than the oxide. This even passivating Ag_2O is converted to the chloride and the sulphide if these components are present in solution.

In addition, the relative solubilities in water are important. Ag_2O is more soluble in water than both Ag_2S and AgCl (Table 3). Thus, the tiny amount of dissolved Ag^+ ions in equilibrium with the passive Ag_2O in water will certainly react with any sulphide associated with the moisture to precipitate Ag_2S. Indeed, dissolved AgCl would also precipitate as Ag_2S with any sulphide present. Now, with continuous moisture present, the precipitation of Ag_2S from dissolved Ag^+ would have 2 further effects. First, more Ag_2O would dissolve to re-equilibrate the oxide with water. Second, precipitation of Ag_2S would reduce the sulphide content of the moisture, so more H_2S from the atmosphere would dissolve into the moisture film. This process is therefore self-perpetuating, albeit slowly, with gradual deposition of Ag_2S onto the surface from the solution phase.

Now, silver does indeed passivate in water or moist air by oxide film formation and growth according to the passivation reactions above, provided the environment is appropriate to passivation and to maintaining passivity. However, it is not always easy for silver (in particular) to maintain the state of passivity, for which there are several reasons. Briefly, these can be listed as follows.
(i) Silver forms dissolved complexes with many solution ligands. Such complexes, as occur for example with ammonia, cause dissolution of the oxide film.
(ii) Silver forms stable solid compounds with many anions, (such as SO_4^{2-}, CO_3^{2-}, Cl^- and S^{2-}). These compounds are sometimes more stable than Ag_2O, and are therefore formed by reaction of the oxide itself. Ag_2S and AgCl are also less soluble in neutral water than Ag_2O, and this too, enhances transformation of Ag_2O into the tarnish compounds. Such surface compounds are generally not strictly-speaking, passivating, although the rate of transformation can become very low.
(iii) Silver halides are sensitive to light, ie, they are photosensitive, particularly to ultraviolet light. This phenomenon can cause reduction of solid silver compounds back to the metal. Where this occurs, the solid compound darkens through various shades of grey to black, and causes the “tarnish”. The darkening is due to the presence of metallic silver in the surface compound. The presence of oxygen would of course result in re-oxidation of the photo-reduced metal particles, provided they are accessible.

Such reduction reactions are unlikely to form large crystals of metallic Ag in the tarnish, but must be in nanocrystalline form. If such behaviour occurs under the action of light on the passivating oxide film, the process would be destructive to that oxide: what should appear as a thin invisible passivating oxide film (Ag_2O) would now show reduced metal atoms and AgCl, causing nanocrystallisation. The metallic nanocrystals are then able to react oxidatively with suitable ions in solution, forming AgCl, Ag_2S etc, as a corrosion product, and that would disrupt the passivity. Even if passivation then succeeds, this process would require further metal oxidation from the surface, and the corrosion product would thereby thicken slowly.

The behaviour of small particles can be very different from that of larger particles. This arises at least in part, from the fact that the ratio of surface area to volume in nanoparticles is relatively high, that is to say, that a significant fraction of the total number of atoms in such a particle are in fact surface atoms. Surface atoms carry unsatisfied bonding, and are therefore more reactive than bulk atoms, ie they would be expected to show a lower equilibrium potential for electrochemical reactions. The phenomenon has been studied extensively, both from practical as well as theoretical viewpoints (14,31-33). Nanoparticles of metallic silver are therefore expected to be reactive with the environment, and indeed, have been shown to grow “tarnish” layers more quickly than bulk silver (14).

The formation of Ag_2S, the main constituent of atmospherically formed tarnish on Ag, is complex. The simple reactions 21 and 22 are long understood, with the cathodic reaction required for these to occur is being reduction of atmospheric oxygen. The surface sulphide is well characterized, but there are many complications. For example, the formation of Ag_2S in the atmosphere can be caused by other compounds of S, such as SO_2. SO_2 is a widely distributed atmospheric sulphurous gas, highly acidic and one of the main components of acid rain. The complex chemistry of sulphur raises the questions of how this can form Ag_2S. The obvious route is through the direct reaction of Ag with SO_2 is not possible in the absence of an oxidizing agent, which would necessarily be O_2.

However, the complexity of the redox reactions of sulphur, and its many possible oxidation states, is such that the reaction of SO_2 in moisture is able to undergo a disproportionation reaction to form both S^{2-} and SO_4^{2-} via:

$$4SO_2 + 6H_2O + 4H^+ \rightarrow S^{2-} + 3SO_4^{2-} + 2H_2O + 12H^+ \qquad (30)$$

This disproportionation reaction is viable at normal ambient temperatures with a standard free energy of reaction, $\Delta G°_f$ = -167.6 kJ/mol of reaction as written here. Here, a single oxidation state of sulphur (IV) reacts to give two oxidation states of sulphur (-II) and (VI), and that reaction is favorable, requiring only water. It may be questioned, then, why SO_2 is such a common pollutant, when it is thermodynamically unstable relative to its own reaction products as in reaction 30, which should occur naturally. The answer to this must lie in the fact that the reaction is a redox reaction, with S in SO_2 being both oxidised and reduced, and this requires electron transfer from 1 molecule of SO_2 to another. The reaction is likely to be extremely slow without the presence of a catalyst, and that catalyst would likely be the metal surface, functioning as an electron conductor as well as a site of high adsorption coverage. For this reaction to proceed as written requires 4 SO_2 molecules to come together (in the ambient gas phase, or in aqueous solution), and the probability of bringing these together would be greatly enhanced by adsorption to the surface. Indeed, simply bringing two SO_2 molecules together for a sufficient time to allow electron transfer between their 2 S atoms seems rather improbable, and then could only form intermediates in the reaction. The presence of the Ag surface allows the electrons from the S in one adsorbed SO_2 molecule to be transferred to the S in a completely remote adsorbed SO_2 molecule, with the electron conductivity of the metal surface providing catalyst mechanism. This mechanism is similar to the basic "autocatalytic" mechanism of metal corrosion, where the electron conductivity of the metal catalyses its own corrosion. Here however, it is catalysing the reaction of the sulphur atom. The surface allows 2 remote SO_2 molecules to react without having to come together in a molecular collision. Once transformed, the SO_4^{2-} would be unreactive to the metal, and desorb (or perhaps form Ag_2SO_4 as part of the embryonic tarnish. The S^{2-} could then react directly with the metal, or much more probably, with Ag_2O to form the tarnishing Ag_2S.

Carbonyl sulphide is also a potentially aggressive species in the atmosphere, but its reactions to form Ag_2S are little more obscure. COS is known to decompose in air to H_2S and CO_2, as

$$COS + H_2O \rightarrow CO_2 + H_2S \qquad (31)$$

Using reasonable partial pressures of all the gas phase components of this reaction (see Table 2), it shows a free energy change which is negative (*ca*. -27 kJ/mol), implying spontaneous reaction as written. This reaction must of course be very slow in ambient air, because the permanent concentration of COS is very low (equivalent to ca. 0.5 ppb, or nbar). However, the reaction is very likely to be catalyzed by the silver surface, even though no electron transfer is involved here. Reactions of this kind are catalyzed by adsorption of the reactants onto surfaces. In simple terms, the adsorbed surface has a higher concentration of the molecules, and is also bound loosely to the surface. Because pairs of molecules then have more time attached onto the surface (the residence time) they can arrange their orientation to facilitate the reaction. It is not clear from published literature whether the COS is able to form Ag_2S by direct reaction, or whether the H_2S formed by reaction of COS with water as above, catalyzed by the surface, then forms the Ag_2S from the H_2S released.

Note that although we consider the reactions of metallic Ag with sulphide (and perhaps chloride) to form the tarnish in the moist system, it must be emphasized that the tarnish is likely to be formed mainly from the reaction with Ag_2O (the passivated surface), rather than with Ag itself, similar to the dry system, albeit more slowly. The reason is that even in the moist system, water and oxygen are the overwhelming components for reaction, with the sulphide being relatively small, and so the metal passivates. However, there are circumstances where this may differ, such as the circumstance where salt spray (Cl^-) has condensed on the surface and evaporated. Here we may accumulate a concentrated salt film, which may prevent passivation.

The action of vapours emitted from wood

Commonly not considered important, wood used for storage of artefacts, such as museum items, can emit acidic vapours. These vapours are aggressive to many metals, including Cu, Zn and Fe. Generally organic acids, these include formic, acetic, propionic, acrylic, caprylic and crotonic acids (23-27,). The type and quantity of these depends strongly on the identity of the wood. Such emissions have been analysed and constitute an aggressive environment for many metals. In addition to silver, metals such as zinc, iron and copper can be corroded by the presence of vapours from wood. Freshly cut wood carries the highest concentrations of the vapours and the fastest emission. However, although it might be considered that older wood should be free from such a problem, some timbers continue to emit over many decades. It is worth noting too, that such organic acids can continue to be emitted from wood over a very long time: although the rate of emission must decline with time, analysis of archeological oak, 1000 years old, still shows significant quantity of acetic acid (27).

The vapours are aggressive towards silver for several reasons. In the first place, these emissions from wood are mainly acidic, and particularly in moist environments, they can dissolve the oxidized silver as Ag^+ in the thin layer of moisture which occurs on the surface. Surface films which are porous are particularly bad for that because the condensation of moisture to form liquid water can be enhanced within nanopores, sometimes referred to as capillary condensation. (Capillary condensation of a liquid in minute pores occurs significantly below then saturation vapour pressure.) Most compounds of the simple organic acids with silver, such as silver formate, acetate and propionate have a significant but small solubility in water (0.067M, 0.061M, 0.047M respectively at 20 °C (12)). Once dissolved, they can then precipitate much more slowly by reaction with trace amounts of H_2S, COS and Cl^-, which may accumulate in the surface moisture. It is then easy to see why some organic salts have also sometimes been detected in analysis of tarnish layers. These compounds crystallise during a drying cycle, and they would form tiny crystals (nanocrystals) which would again react with the sulphur- and chlorine-containing gases to form the tarnish. Such crystalline materials are not protective: once crystalline, they cannot form a passivating oxide because they have precipitated from the dissolved state in solution. The gaps between the crystals can also be sites of capillary condensation.

Nanoparticulate silver

The importance of understanding corrosion and tarnishing of silver lies well beyond the usual aspects of decorative appearance and lustre, and the permanent preservation of archaeological artefacts. Silver is used in various forms in sensors (35), in microorganism control (36,37), in cancer treatment (38,39) and in heterogeneous catalysis (40,41) much still under investigation and development. Many such applications involve the metal in particulate form, of sub-micrometre to nanometre dimensions. Now, the appearance of such nanoparticles may not be of importance, and indeed, any tarnish may not even be visible. However, the dimensions of such silver particles casts a new aspect to the problems described above in relation to tarnishing, because the thickness of tarnish can be typically of the same order as the dimension of the silver particles. Metallic nanoparticle of these diemnsions may thus in principle transform or disappear completely by corrosion, or nearly so, or may simply tarnish to completion, turning a Ag nanoparticle to a Ag_2S nanoparticle. In addition, that reaction may be rapid because there is so little metal to react within each nanoparticle.

When dealing with the properties of nanoparticles, it is important to understand that even the thermodynamics of reactions are now altered. The reason for this is the fact that surface atoms are differently bound to the bulk from that of atoms within the bulk. The presence of “dangling bonds” at the surface describes this. Normally when a surface atom reacts to form a new phase, it does so with the formation of a new surface atom, previously below the surface, and it is therefore the property of the bulk metal that is important. To illustrate, one could write this for bulk metal as

$$\mathrm{Ag}x(\mathrm{s}) + \mathrm{Ag}y(\mathrm{b}) \rightarrow \mathrm{Ag}x^{+}(\mathrm{aq}) + \mathrm{Ag}y(\mathrm{s}) + e^{-} \qquad (32)$$

In a simple way, we can envisage that as follows. Two silver atoms, *x* and *y*, are at the surface (s), and below the surface (b) respectively. Only one atom, *x*, can dissolve, since of the two, only *x* is at the surface. Atom *x* then, forms the dissolved ion (or other reacted species), and atom *y* now becomes the surface atom. Since both sides of this reaction contain a surface Ag atom, they cancel out for thermodynamic purposes. The net reaction, and its net free energy change are that of a bulk Ag atom dissolving. In fact, atom *y*, initially just below the surface, also has its energetics affected by being so close to (but below) the surface. However, inclusion of atoms in layers further beneath the surface into the above reaction would also cancel out, validating the above rationale.

Now, if the "bulk" material is in fact a nanoparticle, there is a relatively large ratio of surface atoms to bulk atoms, and there are therefore insufficient bulk atoms for this to occur without change. In other words, most of the atoms in the nanoparticle have their energies affected by the fact that very few would be real bulk atoms, the actual amount depending strongly on the actual dimension of the nanoparticle. This means that the thermodynamics of reactions of the nanoparticle surface are different from that of bulk material, and in fact, they make reaction of the metal easier. The matter has been studied, quantified and modeled by Sieradzki et al (31,32) using platinum nanoparticles to examine the electrode potentials representing equilibria between Pt and oxidized Pt, as:

$$\mathrm{Pt} \rightarrow \mathrm{Pt}^{2+} + 2e^{-} \text{ (metal dissolution)} \qquad (33)$$

and

$$\mathrm{Pt} + \mathrm{H_2O} \rightarrow \mathrm{PtO} + 2\mathrm{H}^{+} + 2e^{-} \text{ (passivation)} \qquad (34)$$

Electrode potentials of these reactions on nanoparticulate materials are all lowered relative to those of bulk materials, by an amount which is related directly to the particle size. The results show a linear decrease in electrode potential with increase in $2/r$, where r is the particle radius. In other words, it is easier to oxidise the metal when in nanoparticulate form, than when it is in bulk form. We expect this same phenomenon for silver as well (indeed, for most metals).

Electronic circuits

Silver has major uses in electronic circuits as an interconnect, and often circuits are microcircuits. Interconnects can be of very small dimension, and their sole use is simply to conduct electrons from one component to another. As such, they are often very thin, and any tarnishing can cause a change in the conductance. It is a problem of particular interest from a tarnishing perspective because the thickness of a tarnish layer can be of order similar to the dimension of the interconnect itself. In addition, because the interconnect carries current, it hold a voltage, and an electric field. If corrosion or tarnishing is localized on the surface, this can cause the local electric field to rise, and this can give rise to generation of metal needles growing from one contact to another: growth of such metal needles causes electric short-circuit and component failure. This problem is not unique to silver, but it is a property of silver.

Although the mechanism of needle growth is unclear, it is known to be exacerbated by tarnishing.

Combatting tarnish layers

(i) Cathodic reduction of tarnish

The fact that compounds of silver are easily reduced electrochemically back to the metal makes possible methods of cleaning easy to conceive. Reactions such as:

$$AgCl + e^- \rightarrow Ag + Cl^- \qquad (35)$$

$$Ag_2S + 2e^- \rightarrow 2Ag + S^{2-} \qquad (36)$$

occur readily at electrode potentials that are not too low, and are facile. As an example, the work of Degrigny et al (42) is cited. Such work however, requires great care, and full understanding of what is being done. Electrolysis requires the use of an electrolyte, and this requires careful consideration. Many components are themselves reactive towards the metal, either through their oxidizing action, or through their ability to complex with oxidized Ag^+ ions. For example, Degrigny et al (42) use $NaNO_3$ solution in a citrate buffer, pH = 4.8. The nitrate anion is however, a powerful oxidizing agent, and while unpolarised, the metal must be oxidised chemically. In addition, the NO_3^- anion is itself electrochemically active, and can undergo facile cathodic reduction. A wide range of reduction products can be formed electrochemically by cathodic reaction of NO_3^-. These involve a range of oxidation states of the N component: NO_2, NO_2^-, NO, N_2O, N_2 and NH_3. One such cathodic reduction product is ammonia, and the NH_3 species is a powerful complexant for Ag^+ ions, stabilizing the oxidised metal as its dissolved ion. (Exactly analogous reactions occur on copper, which is also oxidized by the nitrate anion, and whose cations in both Cu(I) and Cu(II) form are strongly complexed by any ammonia that might be formed from these reactions.) Electrochemical reduction should ideally be carried out in an electrolyte containing unreactive salts, whose dissolved ions serve only to carry electrolytic current.

(ii) Cathodic reduction of tarnish by electroless means

Reduction of the tarnish layer by contacting the silver with aluminium in a suitable solution (typically aqueous sodium bicarbonate) has been long known. Such reduction is achieved without applying voltage from an external source, because the aluminium functions as a sacrificial anode, thereby providing the electrons to the Ag cathode. It is sometimes erroneously reported that the reaction involves the formation of aluminium sulphide (Al_2S_3): this is utterly wrong. No Al_2S_3 can be formed in this process, for several reasons. It is the use of an alkaline solution ($NaHCO_3$), which allows Al to dissolve anodically, while passing the electrons to the Ag. Thus correctly, we would write anodic reaction for that as:

$$Al + 2H_2O \rightarrow AlO_2^- + 4H^+ + 3e^- \qquad (37)$$

The electrons from this reaction would then be released to the silver to reduce the tarnish via reactions 35 and 36. In fact, this process is directly comparable with the engineering procedure of cathodic protection of steel structures by use of a sacrificial anode, and indeed, alimunium anodes are sometimes used for that purpose.

(iii) Application of inhibitors

Inhibitors of corrosion are exactly that: they inhibit corrosion, ie they retard the corrosion rate, but they do not prevent corrosion. The distinction is important. Inhibitors can be used to control the rate of tarnishing, but in one of two ways only. If the metal is stored in a closed environment, then a vapour phase inhibitor can be used in that environment. Alternatively, an inhibitor can be incorporated into coatings applied to the surface to protect it. The mechanism of action of corrosion inhibitors is still under much dispute: there are probably many such mechanisms operating on different parts of the reaction. The simplest action of a corrosion inhibitor is its adsorption to the surface, blocking the contact between the metal and its environment. Very many papers have been published to this effect, and the data are proposed to fit with isotherms describing the thermodynamics of the adsorption process. Although several isotherms have been shown to adequately fit the data, the fit can only be regarded as fortuitous. The most common isotherm demonstrated is the Langmuir isotherm. Originally used to describe the adsorption of simple gases to ceramic surfaces, the isotherm has been frequently applied to electrochemical systems. However, there are inherent flaws in this interpretation, and in the application of inhibitors, this is particularly pronounced.

Once adsorbed, the inhibitor must then also have a role in interfering with the corrosion or tarnishing reaction, either in the aqueous phase, or in the gas phase. There are several ways this can potentially occur.

The notion of complexing the surface atoms with a suitable ligand which simultaneously protects the surface has been known for a long time from a practical perspective. Amine groups are known complexants for Ag(I), most notably, ammonia itself. (The same is true for copper.) Normally, such complexants would cause corrosion, by stabilizing the oxidized metal ions in the aqueous phase. This leads to severe corrosion of Ag and Cu (and Zn) in solution, as well as giving rise to a classical form of stress-corrosion cracking (in brasses). Such reactions stabilize the dissolved ion relative to any passivating oxide that may otherwise protect the metal. However, some work carried out many decades ago showed that in a confined atmosphere, a volatile organic amine functions as a remarkably effective corrosion inhibitor for Ag: the methodology was patented by Briggmann in 1943 (43). The formation of a complex was recognized in a subsequent patent by Kamlet (44) as requiring formation of a surface complex. Kamlet pointed out that an aqueous solution of the organic amine would be of limited use in a confined atmosphere, so Kamlet’s method used similar organic amine molecules, but held in solution with other organic solvents, inert to the silver. The most rational ones proposed involved no liquid-phase in the ambient solution (and thereby no water) in the system. The work required that the amine sublimed from the solid solution, but the other components did not. Thus compounds such as morpholine (a heterocyclic aliphatic amine) dissolved in trioxane, p-dichlorobenzene, camphor etc were tested and found to function well.

The method is particularly clever because it relies on the strong interaction between the ligand and the (presumably) oxidized metal cation. In the cases mentioned above, the strength of the ligand is due to its lone pair of electrons on the N(III) atom. By complexing with the oxidized Ag^+ cation, but also retaining it on the surface of the metal, the remaining part of the ligand (ie the end without the N atom) then faces the environment. Several issues then arise:

(i) The ligand retards or prevents access to the Ag by the dissolved ions or aggressive species (Cl^- and S^{2-}).
(ii) If the remaining part of the ligand molecule is simply a hydrocarbon, it would render the surface hydrophobic, minimizing water access. This would also minimize access of ions, since hydrophobic molecules generally repel ions.
(iii) Such ligand complexes may also form solid compounds which effectively passivate the metal surface.

We note that there is clearly much potential for developing surface layers using such complexants. Ag^+ cations are complexed by many ligands, with the lone electron pair on trivalent organic N being particularly suitable. The phenomenon has been applied in many fields, for example, in the study of a new class of possible antibiotics, and in their potential anti-cancer activity, using nitrogen heterocyclic carbenes to complex the Ag^+ ion. Some of these complexes employ pincer-type ligands, which grasp the Ag^+ ion like a claw or talon, and appear to be relatively stable. If such ligands can be made to complex with the cation, and bind to the surface as well, then suitable design of the ligand backbone should render it protective. Protection by using a hydrophobic backbone would be one approach.

(iv) Alloying

Experiments into preventing tarnishing of silver using different alloying elements have been reported over many decades. Such methods are clearly inappropriate to preservation of existing silver objects, although can be made useful for the further application of the metal. Sterling silver, containing 92.5 wt% Ag, is not useful as a tarnish resistant alloy of silver, because its main alloying element, Cu, is as prone to tarnishing as silver itself. Indeed, the chemical properties of Cu are very similar to those of Ag, both chemically and electrochemically, but with the added disadvantage that Cu is a more base metal. As early as 1932 (45) some success was found. There is no doubt that some of these are effective in retarding the development of a tarnish layer. Diverse elements such as In, Sn, Pd, W, Y etc have been shown to provide resistance to tarnishing, although such resistance is not necessarily permanent. A great deal of improvement is possible by examining the mechanisms by which minor element compositions of alloys can play a large role in controlling the

(v) Surface alloying

Surface alloying is a means of creating a tarnish resistant metal, without changing the bulk properties of an existing article. Methods for doing this have proliferated in recent decades.

Conclusions

The tarnishing of silver is a natural process cause by the highly sensitive reactions between the metal and aggressive components of the environment. Tarnishing is a complex process with many sensitive variables. In general, the aggressive environmental components are sulphur-containing and chlorine-containing vapours. In the absence of aggressive species, silver would normally passivate in air, dry or moist, by formation of silver oxide, Ag_2O, and in the absence of aggressive contaminants, should remain bright. This oxide is passivating, in that its growth retards further oxidation to a minimal level. Tarnish forms by aggressive components of the environment (carrying sulphide and chloride) attacking the Ag_2O, and perhaps the metal itself, by formation of the sulphide and the chloride. The passivating properties of the oxide films are thereby degraded, although the corrosion rate is low.

The tarnish occurs because Ag_2S, and to a lesser extent AgCl, are far more stable than Ag_2O. This does not mean that Ag_2S and AgCl form first. In normal environments, the pressures of sulphur-containing gases is very much lower that oxygen in air, so the oxide must form first. The sulphide and chloride then form much more slowly, and therefore do so by reaction with the oxide itself. The reaction of sulphide with the metal itself is not a necessary condition for tarnishing to occur.

Because of the fact that oxygen is the overwhelming pressure of reacting gas, it must be that the oxide forms first on the metal when freshly exposed. The tarnish occurs by reaction of sulphur- and chlorine-bearing gases, particularly the former, which convert the oxide to sulphide (and chloride). The transformation of the passivating oxide to the black sulphide is the fundamental tarnish reaction, in both wet and dry conditions.

Formation of the sulphide from the chloride is thought to induce crystallisation of the surface layers, with associated defects, and also, to generate further defects in the crystals themselves. The depassivated areas of the surface would react rapidly again with oxygen in the environment to produce more Ag_2O. This would then be converted to silver sulphide, but more slowly. Particularly the sulphide is very stable. This causes Ag_2S to form even when the sulphur component of the environment is of very low pressure, but the kinetics are slow. Both H_2S and COS are responsible, although SO_2 also causes Ag_2S formation when the environment is moist.

The tarnish reactions are all greatly accelerated by moisture. They are also accelerated by the presence of other environmental contaminants, such as acidic vapours emitted by wood, which are aggressive towards silver, as towards many metals.

Electrochemical experiments show that the chloride ion enters the first stages of filming, contributing AgCl to the first monolayer of AgOH and Ag_2O as they form: however, relatively high concentrations of chloride are required to be able to observe this. We deduce that sulphide ions would do the same, but this has not been tested. These concentrations of Cl^- are comparable with those which could accumulate from sea-spray, but not compatible with a non-marine, gaseous environment.

The problems of tarnishing are much higher when the target material is nanoparticulate. Under these circumstances it would seem possible for the entire metallic nanoparticle to be converted to Ag_2S.

Because of the many steps involved in the tarnishing process, there are also many potential parts of the reaction with which to interfere, when inventing or designing combative methods. These include appropriate alloying, either in bulk, or as a surface alloying procedure. Understanding the passivity of passive alloys is a good step towards this goal.

References:

1. B.H. Chudovsky. Degradation of power contacts in industrial atmosphere: silver corrosion and whiskers. Proc. of the 48th IEEE Holm Conf. on Electrical Contacts. 23 Oct 2002, Orlando, USA, IEEE (2002).

2. B.T. Reagor, J.D. Sinclair. Rapid tarnishing of silver nanoparticles in ambient air. Appl. Phys. B – Lasers and Optics, 80 (2005) 915-921.

3. R. Weisinger, I. Martina, Ch. Kleber and M. Schreiner. Influence of relative humidity and ozone on atmospheric silver corrosion. Corros. Sci., 77 (2013) 69-78.

4. X. Bao, M. Muhler, B. Pettinger, Y. Uchida, G. Lehmpfuhl, R. Schlögl and G. Ertl. The effect of water on the formation of strongly bound oxygen on silver surfaces. Catal. Letters, 32 (1995) 171-183.

5. T.E. Graedel. Corrosion mechanisms for silver exposed to the atmosphere. J. Electrochem. Soc., 139(7) (1992) 1962-1970.

6. S. Bouquet, C. Bodin, C. Fiaud. Relative influence of sulphide and chloride compounds on tarnishing of silver in atmospheric corrosion. Comptes Rendue de l'Academie des Sciences Serie III, 316(4) (1993) 459-464.

7. K. Hallett, D. Thickett, D.S. McPhail, R.J. Charter. Application of SIMS to silver tarnish at the British Museum. Appl. Surf. Sci., 203 (2003) 789-792.

8. H. Kim. Corrosion process of silver in environments containing 0.1 ppm H_2S and 1.2 ppm NO_2. Mater. Corros. 54 (2003) 243-250.

9. H.A. Ankersmit, N.H. Tennent, S.F. Watts. Hydrogen sulphide and carbonyl sulphide in the museum environment – Part 1. Atmospheric Environment 39(4) (2005) 695-707.

10. D. Liang, H.C. Allen, G.S. Frankel, Z.Y. Chen, R.G. Kelly, Y. Wu, B.E. Wyslouzil. Effects of sodium chloride particles, ozone, uv, and relative humidity on atmospheric corrosion of silver. J. Electrochem. Soc., 157(4) (2010) C146-C156.

11. K.A. Folgner, C.T. Chu, Z.R. Lingley, H. Kim, J.M. Yang, J.D. Barrie. Environmental durability of protected silver mirrors prepared by plasma beam sputtering. Appl. Optics, 56(4) (2017) C75-C86.

12. R.C. Weast (Editor). Handbook of Chemistry and Physics, 57th edition, CRC Press, Cleveland, Ohio (1976).

13. M. Pourbaix. Atlas of Electrochemical Equilibria in Aqueous Solutions. Pergamon/CEBELCOR (1966).

14. M. McMahon, R. Lopez, H.M. Meyer, L.C. Feldman, R.F. Haglund. Rapid tarnishing of silver nanoparticles in ambient laboratory air. Appl. Phys. Letters B – Lasers and Optics, 80(7) (2005) 915-921.

15. K. Kourtidis, A. Kelesis and M. Petrakakis. Hydrogen sulphide in urban ambient air. Atmos. Environment, 32 (2008) 7476-7482.

16. C-H. Selene and J. Chou. Hydrogen sulphide: human health aspects. Concise International Chemical Assessment Document 53, p. 14, World Health Organization, Geneva (2003).

17. J.R. Duncan, J. Balance. Marine salts contribution to atmospheric corrosion. In “Degradation of Metals in the Atmosphere”, Editors: S. Dean and T. Lee, ASTM International (1987), pp316-325.

18. G.T. Burstein and R.C. Newman. Anodic behaviour of scratched silver electrodes in alkaline solution. Electrochim. Acta 25(8) (1980) 1009-1013.

19. G.T. Burstein and R.C. Newman. Scratched silver electrodes in perchloric acid solution. Electrochim. Acta, 26(8) (1981) 1143-1145.

20. G.T. Burstein and D.H. Davies. The electrochemical behavior of scratched iron electrodes in aqueous solution. J. Electrochem. Soc., 128(1) (1981) 33-39.

21. G.T. Burstein and D.H. Davies. The effects of anions on the behaviour of scratched iron electrodes in aqueous solutions. Corros. Sci., 20(10) (1980) 1143-1155.

22. G.T. Burstein and R.C. Newman. Reactions of scratched copper electrodes in aqueous solution. J. Electrochem. Soc., 128(11) (1981) 2270-2276.

23. 5. P.C. Arni, G.C. Cochcrane, J.D. Gray. Emission of corrosive vapours from wood. 1: Survey of the acid release properties of certain freshly felled hardwoods and softwoods. J. Appl. Chem. 15(7) (1965) 305-313.

24. W. Sandermann, U. Gerhardt and G. Weissmann. Untersuchungen über Flüchtige organische Säuren in einigen Holzarten. Holz roh- und Werkstoff, 28 (1970) 59-67.

25. L.T. Gibson and C.M. Watt. Acetic and formic acids emitted from wood samples and their effect on selected materials in museum environments. Corros. Sci., 52 (2010) 172-178.

26. L.T. Gibson, B.G. Cooksey, D. Littlejohn, N.H. Tennent. A diffusion tube sampler for the determination of acetic and formic vapours in museum cabinets. Analyt. Chim. Acta, 341 (1997) 11-19.

27. J. Glastrup, Y. Shashoua, H. Egegaard and M.N. Mortensen. Formic and acetic acids in archaeological wood. A comparison between the Vasa Warship, the Bremen Cog, the Oberländer Boat and the Danish Viking Ships. Holzforschung, 60, (2006) 259-264.

28. G.T. Burstein and B.T. Daymond. The remarkable passivity of austenitic stainless steel in sulphuric acid solution and the effect of repetitive temperature cycling. Corros. Sci., 51 (2009) 2249-2252.

29. G.T. Burstein and R.D.K. Misra. Electrochemistry of scratched silver electrodes in chloride solutions. Electrochim. Acta, 28(3) (1983) 363-369.

30. G.T. Burstein and R.D.K. Misra. Growth of oxidised monolayers on scratched silver electrodes in chloride solutions. Electrochim. Acta 28(3) (1983) 371-377.

31. L. Tang, B. Han, K. Persson, C. Friesen, T. He, K. Sieradzki and G. Ceder. Electrochemical stability of nanometer-scale Pt particles in acidic environments. J. Amer. Chem. Soc., 132 (2010) 596-600.

32. L. Tang, X. Li, R.C. Cammarata, C. Friesen and K Siedradzki. Electrochemical stability of elemental metal nanoparticles. J. Amer. Chem. Soc., 132 (2010) 11722-11726.

33. O.S. Ivanova and F.P. Zamborini. Size-dependent electrochemical oxidation of silver nanoparticles. J. Amer. Chem. Soc., 132 (2010) 70-72.

34. S.L. Zelinka and D.S. Stone. The effect of tannins and pH on the corrosion of steel in wood extracts. Mater. Corros., 62(8) (2011) 739-744.

35. J.C. Reed, H. Zhu, A.Y. Zhu, C. Li and E. Cubukcu. Graphene-enabled silver nanoantenna sensors. Nano Lett., 12 (2012) 4090-4094.

36. C-N. Lok, C-M. Ho, R. Chen, Q.Y. He, W.Y. Yu, H. Sun, P. Kwong-Han, J-F. Chu and C-M Che. Silver nanoparticles: partial oxidation and antibacterial activities. J. Biol. Inorg. Chem., 12(4) (2007) 527-534.

37. S. Sarkar, C.A. Kumar, P. Kumbarkhar and T. Mandal. Aqueous synthesis and antibacterial activity of silver nanoparticles against pseudomonas putida. Materials Today: Proceedings 11(2) (2019) 686-694.

38. S. Yesilot and C. Adin. Silver nanoparticles: a new hope in cancer therapy? Eastern J. Med., 24(1) (2019) 111-116.

39. Y. Ma, L. Shi, F. Liu, Y. Zhang, Y. Pang and X. Shen. Self-assembled thixotropic silver cluster hydrogel for anticancer drug release. Chem. Engng. J., 362 (2019) 650-657.

40. J.M. Linge, H. Erikson, J. Kozlova, J. Araväli, V. Sammelselg and K. Tammeveski. Oxygen reduction on electrodeposited silver catalysts in alkaline solution. J. Solid State Electrochem., 22(1) (2018) 81-89.

41. F. Muench, R. Popovitz-Biro, T. Bendikov, Y. Feldman, B. Hecker, M. Oezaslan, I. Rubinstein and A. Vaskevich. Nucleation-controlled deposition of silver nanoplate architectures for facile derivatization and catalytic applications. Advanced Materials, 30(51) (2018) 1805179.

42. C. Degrigny, R. Jeanneret, D. Witschard, C. Baudin, G. Bussy, H. Carrel. A new electrolytic pencil for local cleaning of silver tarnish. Studies in Conservation 61, (2016) 162-173.

43. G.F. Briggmann. Method for preventing silvertarnish. US Patent no. 2323369A, July 6th (1943).

44. J. Kamlet. Method of protecting metallic surfaces against tarnishing and corrosion. US Patent no. 2,475,186, July 5th (1949).

45. K.W. Ray, W.N. Baker. Tarnish-resistant silver alloys. Industrial Engineering Chemistry 24 (1932) 778-781.