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New Model of Outdoor Bronze Corrosion and Its Implications for Conservation

Luc Robbiola and Christian Fiaud

Centre National de la Recherche Scientifique, Unité 216
Ecole Nationale Supérieure de Chimie de Paris,
Corrosion Laboratory
11 rue Pierre et Marie Curie
F -- 75005 Paris

Stéphane Pennec

LP 3 Conservation
8 rue des Tanneries
F -- 21140 Semur en Auxois

Abstract

A new model that takes into account both the tin and the copper in the alloy is proposed to improve the understanding of deterioration processes of outdoor bronze sculptures. The corrosion mechanism relates to the selective dissolution of copper. Two main processes occur: the process of tin oxidation with the formation of insoluble tin compounds which remain in the corrosion film, and the process of copper oxidation with the migration of copper ions to the surface. Considering this mechanism, mechanical action, and the acidity of the precipitations, two different evolutions at the surfaces are suggested. On the surfaces directly exposed to the rain, copper ions are washed out leaving a tin-rich external layer. A cyclic corrosion process is engaged. In the unexposed surfaces, the outermost layer is formed with well-known copper corrosion products.

This model can be used to establish the degradation state of outdoor bronze sculptures for a new conservation approach.

Keywords

Atmospheric corrosion, bronze, conservation, corrosion products, outdoor sculpture

Introduction

The purpose of this present paper is to outline a general framework for the understanding of the corroded surfaces of outdoor bronzes. Due to the increase in the pollution level of the atmosphere, the patinas on outdoor bronzes are now generally unstable. This can be observed by green trails on the stone basements due to the dissolution of copper. Numerous papers explain the bronze corrosion process by applying the copper corrosion model which leads to the following corrosion structure: a green outermost layer of copper II compounds (generally hydroxysulfates) and an internal layer of copper oxide located on the unattacked alloy^[1-3].

The model described here was established from several investigations of outdoor bronze sculptures such as Rodin's bronzes, a Stanislas statue in Nancy, France, and other bronzes exposed to urban atmospheres^[4-6]. In these studies, different analyses were performed to correlate the nature of the corrosion products and their location with exposure conditions. The nature of patinas and their chemical characteristics will be reviewed first. Then, this information will be used to propose a qualitative mechanism for the growth of corrosion layers.

Some aspects of the problem cannot be presently specified with rigor. The semi-quantitative assessment of the formation of corroded surfaces represents a step towards a more complete understanding of the corrosion processes. This paper will make frequent reference to published works on copper patina formation^[7].

The nature of corrosion products

Analysis of corrosion products on outdoor bronzes (Cu-Sn alloys) revealed numerous copper compounds which have their own characteristics, depending on surface orientation and the conditions of atmospheric exposure. Characterization of the corrosion products' thermodynamic stabilities and research on their formation kinetics have already been published^[8-11]. Little is known about the corrosion products of tin. They are generally not identified in the bronze patinas. Nonetheless, recent results^[4,5,6] show that the corroded surfaces may be classified in relation with their aspect (colour, morphology, hardness) and composition. The different surface categories are related to the rainfall exposure conditions. The results are summarised in Table 1.

Two types of surfaces may be distinguished: those exposed to rainfall, and those protected from this effect. The first category in the table lists results for surfaces exposed to rainfall. They are made of pale green products and black areas which stand as islands surrounded by the pale green products (Figure 1). As already mentioned by Weil *et al.*, the pale green areas act as anodes and the black areas act as cathodes^[12]. Elementary analysis reveals that the surface compounds have a high tin element content. X-ray diffraction or infrared spectrometry analysis show that the copper compounds are mainly brochantite and seldom antlerite. The second category in the table outlines results for the surfaces that are not



Figure 1. Macroscopic view of black spots surrounded by green pale corrosion products, porous and unprotected.

Table 1. Comparison between main types of corroded surfaces of the outdoor bronzes exposed in urban areas. The compositions are given in weight percent.

	Composition of the alloy	Main types of corroded surfaces			
		Areas washed by the rainwater		Areas not washed by the rainwater	
		Pale green to blue (porous)	Black (compact, very hard)	Green (compact, ± hard)	"Opaque" black (hard)
Rodin's statues Paris [4] (1880-1920)	Cu (base) 3.6Sn 1.3Zn	mainly brochantite and cuprite (Sn/Cu = 0.8 ± 0.3)	brochantite, organic compounds (?) (Sn/Cu = 0.2 ± 0.1)	brochantite, gypsum, often antlerite, sometimes atacamite (Sn/Cu = 0.08 ± 0.07)	antlerite, gypsum, organic compounds (?), atacamite, brochantite (Sn/Cu = 0.02 ± 0.02)
Des Boers Quebec [5] (1905)	—	—	—	mainly brochantite, some atacamite and cuprite (Sn/Cu = 0.22)	brochantite, antlerite, atacamite, nantokite, cuprite, cassiterite (Sn/Cu = 0.014)
G.E. Cartier Quebec [5] (1920)	—	—	—	mainly brochantite, antlerite, cuprite and some atacamite (Sn/Cu = 0.25)	antlerite, brochantite, atacamite, nantokite, cuprite, cassiterite
Mgr de Laval Quebec [5] (1908)	—	brochantite and cuprite (Sn/Cu = 1.56)	—	brochantite, cuprite (Sn/Cu = 0.24)	—
Le Triomphe de la Republique [6] Paris (1889)	88.4Cu, 4.3Sn, 5.3 Zn, 1.4Pb	mainly brochantite (Sn/Cu = 0.8 ± 0.3)	—	antlerite, brochantite, sometimes atacamite	—
Stanislas Nancy (1831)	61Cu, 4Sn, 14.5Zn, 20Pb	brochantite, cuprite (Sn/Cu = 0.7 ± 0.1)	—	antlerite, quartz, gypsum, organic compounds? (Sn/Cu = 0.04 ± 0.03)	brochantite, quartz, organic compounds? (Sn/Cu = 0.01)



Figure 2. View of a bronze surface not exposed directly to the rain. The green compounds are partially recovered by "opaque" black crusts.

exposed to the rain. They are generally green deposits and/or opaque black crusts^[3]. These crusts (Figure 2) contain various incorporated atmospheric particles and are often found above the green deposits. Compared to the first group, these corrosion compounds have a low or very low tin elemental content, and X-ray or IR spectrometry reveal that they contain both antlerite and brochantite.

Due to their amorphous nature, tin compounds are very difficult to identify with X-ray diffraction or infrared spectrometry. Variations in the colour or local composition of the compounds have not been considered in this work. They are not characteristics of the corrosion mechanism we will describe. Therefore, the red-brown or "quasi-metallic" grey surfaces or cupric oxide and organic compounds observed or detected will not be considered here^[4].

Results given in Table I confirm that there is apparently no relationship between the exposure time and the nature of outermost corrosion layers. This can be correlated to a quasi-stationary state reached by the metallic materials in atmospheric conditions. The range of time to achieve this condition is decreasing: a bronze obtained its patina in several decades at the beginning of the century, while ten years seems to be actually sufficient in the urban areas of industrial countries^[11]. The results also confirm that although metallic structure relates directly to the alloy content, the Zn and Pb contents of the base alloy appear to have a minor influence on the main characteristics of the corrosion products^[13].

These remarkably constant features reveal that outdoor bronzes have a general corrosion behaviour which is strongly dependent on the washing effect of rain-

water. Moreover, our understanding of corrosion phenomena must take into account the influence of the tin in the alloy. The nature of the outdoor bronze patinas cannot simply be regarded as that of the pure copper exposed to the atmospheric environment.

Qualitative model for patina formation

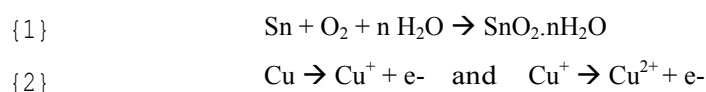
The observed physical and chemical characteristics of the bronze patinas have shown that some constant effects are observed. In order to explain these results, a qualitative model is proposed. This model is based on the formation process model of the corrosion structures observed for buried archaeological bronzes, according to the specific conditions of the atmospheric corrosion^[14, 15].

The corrosion process is essentially caused by a presence of water on the bronze surface. The water on the surface results from precipitation (fog, rain, snow, etc.) or condensation at the metal surface^[10, p. 756]. In the absence of rainfall, the surface water can be assimilated into an electrolyte film whose composition and pH depend on the atmospheric compounds and the soluble corrosion products^[9, p. 724]. Atmospheric corrosion can be regarded as a corrosion process under an electrolyte film. So, by comparison with bronzes partially immersed in an aqueous electrolyte solution, two particularities must be recalled. First, the anodic dissolution products that cannot be evacuated from the surface can easily induce a deposit on the metal surface. This deposit may have either a protective effect if the products are insoluble and homogeneous, or may have an aggressive character if they are soluble and hygroscopic (*i.e.* porous). Secondly, the oxygen reduction rate is greater than that of the usual aqueous electrolyte at the initial stage of corrosion^[11]. Therefore, it appears that the presence of porous deposits has no protective effect. Moreover, these deposits can enhance the dissolution rate of the base alloy. This important point will be considered later in this paper.

Significant amounts of tin products are systematically detected in corrosion products on different bronzes. This result underlines the fact that the Cu-Sn alloy behaviour is more complex than that of the pure copper. Although copper is electrochemically more noble than tin, recent works have shown that for corrosive conditions, such as those of natural environments, the Cu-Sn corrosion behaviour is characterized by selective dissolution of the copper from the alpha phase of the alloy^[14,15]. Copper species can form deposits on the surface, as previously mentioned. In relation to the effect of the rainfall, two types of surface evolutions must be distinguished.

Figure 3 is a schematic diagram of the corrosion process which results in the types of corrosion products described in the previous section. Three main steps are outlined.

The first step is the basic mechanism of the selective dissolution of copper. In contact with the surface water (electrolyte), the oxidation of the alloy can be represented as:



The "tin oxide," stable in aerated conditions and over a large pH range, is cathodic in comparison to the copper. The copper ions produced during the process may build a layer of copper compounds such as cuprous oxide on the top of the surface, while tin compounds remain in the internal part of the corrosion layer.

The second step of the process augments the thickness of the copper deposit by the formation of several copper(II) minerals, the nature of which is greatly dependent on the local atmospheric compositions, *i.e.* mainly brochantite in urban areas or chlorine-containing species in a marine environment. This process is similar to the formation of copper patinas discussed by Graedel^[9, p. 736-738].

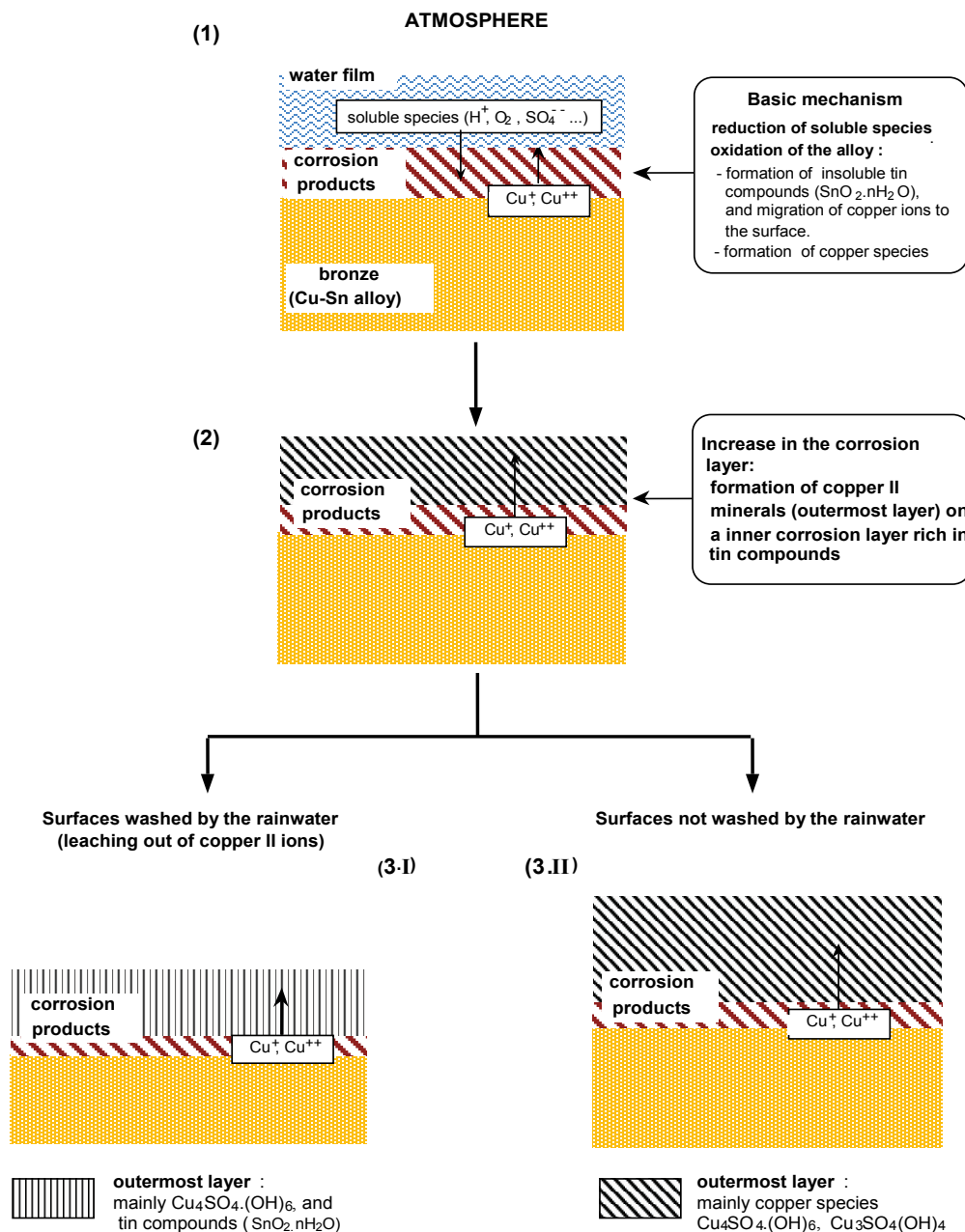


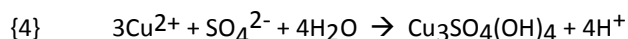
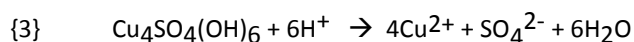
Figure 3. Schematic representation of the processes involved in the outdoor bronze corrosion.

For bronzes, the controlling step of the process is the migration of copper ions from the alloy to the atmosphere through the deposit.

The third step is related to the surface exposure conditions. For actual environments, the acidity of rain and smog can both solubilise the outermost copper corrosion compounds and promote the transformation of minerals. For example, brochantite is transformed into antlerite (this process will be discussed later in the paper). We can distinguish between surfaces directly washed by rainwater (step 3.I) and surfaces which are not exposed to rainfalls (step 3.II).

Soluble copper compounds are leached from the **rain-exposed surface**. The deposit described in the second step is progressively destroyed. The surface is "active" to the main corrosion process (*i.e.* selective dissolution of copper and internal oxidation of tin of the first step). **The corrosion proceeds from a cyclic mechanism that is strongly correlated with the precipitation frequency.** Then, the heterogeneities of the metallurgical structure locally enhance the formation of electrochemical coupling. The surface can be either anodic (pale green areas) or cathodic (islands of black compounds); this is probably related to the microsegregations in the alloy.

The deposit of copper species on surfaces protected from rainfall may be stable, but acidic waters can promote the transformation of brochantite into antlerite (See fig. 3.II). Increasing the acidity of the water film (pH higher than 3.5) leads to the dissolution of brochantite ($\text{Cu}_4\text{SO}_4(\text{OH})_6$) followed by antlerite precipitation ($\text{Cu}_3\text{SO}_4(\text{OH})_4$) in accordance with the reactions:



However, the antlerite formation needs an acidic water layer for a sufficiently long period of time [10, p. 765]. In the case of short acidity periods, which do not allow the growth of antlerite, brochantite can reform on the surface. It is therefore expected that antlerite forms preferentially on the unexposed areas of sculptures that have lower evaporation rates than exposed surfaces.

The scenario developed here explains in a qualitative way nearly all of the results obtained on numerous outdoor bronzes. Nevertheless, this model does not permit one to solve all the problems. One of these problems is that the model is based on a phenomenological approach which can only be used to diagnose the de-graded state but cannot predict the evolution of local patinas on outdoor monuments.

The second point is that the exact process of the transition from Step 2 to Step 3.I is not clearly established. Finally, as mentioned by Graedel, the nature and role of organic species could be very important, but these factors are not yet well understood [9, p. 739].

Application to the conservation of outdoor sculptures

Two main observations can be made based on the model described above. Both aged and recent bronze patinas are now less protective due to air pollution conditions in the environment. Also, the corrosion process is directly related to the presence of water on the metal surface.

Therefore, from the conservation point of view, two conclusions can be drawn. First, it is not relevant to remove the old patina to apply a new one, except to change the aesthetic appearance. Secondly, the conservation of outdoor bronze sculpture involves ensuring a good protection against exposure to water. To this end, conservation treatments may consist of cleaning, passivation, and coating.

Cleaning methods

What should we remove? Dust or "opaque" black surfaces, located on the non exposed areas, must be removed first. These materials form a layer (sometimes more than 5 mm thick) that is very hygroscopic. Not only can these surfaces maintain a high humidity level on the alloy surface, but its black appearance is unaesthetic. Non-compact, pale green corrosion products located on the exposed area are very porous and hygroscopic, and can compromise coating adhesion by their pulverulence.

On the other hand, we can conserve black spots located on the exposed area that delineate the limit of the original surface. However, it is often necessary to remove them for their unaesthetic appearance. Green unexposed areas can be found under the "opaque" black layer. They are not always stable, as is revealed by the transformation of brochantite to antlerite, but they can be considered a good substrate for an applied protective coating.

Several methods have been used for cleaning outdoor bronze sculpture including manual cleaning (scalpel, metal brushes, etc.), electrically operated metal brushes, water pressure tools, water-abrasive, and air-abrasive techniques. Each method can often be used properly, but the most efficient in removal of dust and non-compact corrosion products is certainly the air abrasive method [16]. By varying air pressure, the diameter of the nozzle, and the nature of the abrasive (softness, size, geometry), it is possible to obtain a very good small- and large-scale cleaning. The walnut shell air-abrasive technique (See Figure 4) is widely used for bronze cleaning without stripping [17].



Figure 4. Cleaning of a bronze statue by walnuts shells with an air abrasive technique.

Passivation

There are few corrosion inhibitors available for bronze. Authors have only considered the role of copper and have mentioned the utilisation of benzotriazole (BTA), a copper corrosion inhibitor for outdoor bronze. Is benzotriazole, a good inhibitor for bronze?

There is much to support the use of BTA in the literature. Benzotriazole may build up a three dimensional film with copper, protecting the alloy from outside attack. Turgoose shows that the formation of this film on ancient artifacts happened after a week of immersion in an alcohol bath; obviously, this is not possible for outdoor bronzes ^[18].

Benzotriazole has also been added to such coating systems as microcrystalline wax formulations to increase their quality, such as in microcrystalline wax. For some time, BTA was also added to the famous acrylic resin called Inralac ^[19,20].



Figure 5. Coating of a bronze statue by applying microcrystalline wax on the cleaned surface.

Coatings

Acrylic, polyester, polyurethane, natural wax, and mineral wax have been used as coatings for outdoor bronzes. The characteristics to consider when selecting as coating are life-time, reversibility, aesthetic appearance, and facility of maintenance.

Each chemical family has very different products and it is very difficult to give general recommendations. However, polyurethane can be considered as the best for its life-time (10 years), but it is also the worst for reversibility and facility of maintenance, as it requires complete removal by air-abrasive methods and reapplication for adequate protection. Mineral waxes (microcrystalline) have short lifetimes (2 to 5 years), but have excellent reversibility and maintenance properties. For instance, maintenance consists of a simple water cleaning and application of a new layer. Acrylic has intermediate properties, with a relatively good lifetime, and quite good solvent-reversibility properties ^[20]. It is noteworthy that natural wax can generate acid radicals which increase corrosivity at the surface. None of the coatings are fully convenient, but our choice is oriented to the use of a microcrystalline wax (See Figure 5) with a high melting point because of its facility of maintenance. A two years' maintenance is also good, because it forces people to maintain and to clean their sculptures. Whatever cleaning technique and protection system is chosen, we must be able to understand what should we remove, what should we protect, how much time the coating can be protective, and what is the maintenance process.

Conclusion

The corrosion behaviour of Cu-Sn alloys in outdoor atmospheric conditions is notably more complex than for the pure copper. Though copper is intrinsically a more noble metal than tin, the analysis of corrosion products revealed a tin enrichment; this relates to the formation of tin oxide, which is cathodic to copper. This phenomenon is always observed for bronze corrosion and is attributed to a selective dissolution of copper from the Cu-Sn alloy. If the copper compounds (mainly cuprous oxide and hydroxysulfates) can build a protective and adherent deposit on the surface, the dissolution of the alloy will be stopped. If such a deposit cannot be built up, *i.e.* for areas washed by rainwater, the copper compounds will be leached and the corrosion will proceed by a cyclic mechanism strongly related to the frequency of rainfall.

A new framework is given in this work for understanding the formation of natural patinas. It enables future research to determine the precise mechanism of the destabilisation of the copper compound layers and to improve conservation treatments.

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