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CORROSION AND ANTI- CORROSION PROTECTION OF ARCHEOLOGICAL BRONZE ARTIFACTS

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1. INTRODUCTION

The processes of corrosion may threaten the stability of metal artifact weather we talk about its storage or display . The purpose of this research is the investigation of the efficiency of a set of aminoacids as corrosion inhibitors in the inhibition or prevention of corrosion in archeological artifact made of copper-tin bronzes.

Generally, upon excavation most bronzes are covered in a more or less stable corrosion surface, the "patina" in which both the evenness and stability contribute to the aesthetic beauty of the artifact. However, this outer surface has little in common with the original appearance of the artifact. Corrosion of bronze and copper artifact yielding green patinas is a frequent problem in the fields of archaeometry, conservation and restoration of archaeological objects. Patinas are built in a short period of time, meaning tens of years, with respect to the total burying time that can be thousands of years.

The identification of the corrosion products is not only an essential requisite for selecting the cleaning procedure in conservative and restorative treatment of archaeological pieces, but also an interesting tool for obtaining information on the origin, transport, storage conditions, etc. of such pieces.

Studies on the alteration of copper artifacts have been done for a very long time. At the end of the 19th century, Berthelot recognized the cyclic character of the alteration reaction and identified atacamite, a basic copper chloride, as one of the main alteration products [16], resulting from the presence of corrosive chloride salts. As reviewed by Scott [17], there is general agreement in using the chemical explanation of bronze disease, the formation of cuprous chloride (CuCl, nantokite) playing an essential role in the overall process. This compound may lie dormant until reaction with moisture and oxygen results in the process labeled as bronze disease, in which an extensive corrosion is produced. The detailed processes and conditions involved in copper corrosion remain, however, matter of discussion .

The term inhibitor is derived from the Latin *inhibere*, "to check". Many different experiments have been carried out on artifact to try to prevent further corrosion but some techniques, for example chemical stripping, have caused irreparable damage. In the late fifties and early sixties, certain organic corrosion inhibitors, developed for industry, were tested to try to conserve metal artifact [11]. In order to preserve metal works from corrosion conditions, suitable treatments with coating substances are often required. To this regard, a range of organic products can provide protection to the exposed surfaces by the formation of either thick barrier layers as waxes or polymeric products or thin films for example corrosion inhibitors.

Organic inhibitors normally form very thin and persistent chemisorbed films that lead to a remarkable decrease in the corrosion rate due to the slowing down of the anodic or cathodic reaction or both. The most efficient and well known organic inhibitor on copper is 1,2,3-benzotriazole (BTA) and its derivatives. These substances offer a good protection against corrosion in different aggressive environments [13].

The problem with these substances are their high toxicity and the fact that are not biodegradable. A very good alternative to corrosion inhibition is the use of aminoacids: and environment friendly approach and very efficient in corrosion protection.

2. THEORETICAL AND EXPERIMENTAL ASPECTS

Any metal exposed to environment is going through the process of corrosion. The corrosion product contains a large number of compounds that determine the overall corrosion behavior and appearance of the exposed metal. This slow formation process is the result of a number of chemical, electrochemical and physical processes that occur during the interaction between the metal and the environment. For that reason each metal behaves differently.

Copper is probably the most investigated metal when it comes to corrosion product evolution. The term patina is used to include all compounds in corrosion products formed on copper, irrespective of composition. As the main constituents of bronze alteration layers reported in the literature are copper-containing compounds, bronze corrosion has consequently often been assimilated to pure copper corrosion.

Among the family of ancient metals, bronzes Cu-Sn alloys have been studied for more than a century in view of the surface modifications they have suffered in the course of time. Numerous studies on ancient and historical bronzes have tried to establish the chemical characteristics and structure of natural patinas grown on artifacts exposed for long periods of time to soil, atmosphere, water or sea water. The long-term corrosion of bronzes is accompanied by structural transformations leading to a steady state. Different surface patterns have then been observed depending on the corrosive environment (chemical composition, pH, etc) but also on other non-negligible parameters such as historical periods, metallurgical techniques or even kind and size of the artifact itself. [12,14]

It must be noticed that in the case of artefacts found in archaeological soils, chemical composition and properties (pH, buffer capacity) of soils have been modified with time, and that both climate and activity on the site have changed. The present environmental factors are apparently of greater importance when recent modifications of soil are encountered. Studies have shown that correlations exist between the alterations suffered by bronze artifacts and their actual environment in terms of geology, geography, local or distant polluting sources, and their archaeological context: type of site, depth of burying [12,15].

Robbiola et al [12] have found that in an oxygenated corrosive medium the main phenomenon involved in bronze corrosion is copper selective dissolution from the copper solid solution, in other words, the corrosion process is due to decuprification and not to destannification as considered before.

Two types of microstructures have been identified and characterized [12]:

Type I structure or "even surfaces” can be ascribed to internal tin oxidation, accompanied by selective copper dissolution.

Type I surfaces layers are very protective and are of different colors: blue, green to dark green, dark grey or in some cases metallic grey. They appear generally shiny and lustrous and are often called noble patina.

In Type II structures or "coarse surfaces” the corrosion process is assumed to be controlled by mass transportation of negative species from the soil , mainly oxygen and chloride ions.

Type II surfaces result from localized corrosion phenomena, but also from generalized attacks due to a high dissolution rate. Type II surfaces are rough and their color may be red, brown or more often green.

It is considered that the initial step of the corrosion process is the dissolution of the alloy surface after it was buried into the soil, despite the fact that some corrosion| of the artifact may have existed before its burial. Depending on the rate and the homogeneity of the attack the alloy oxidation will lead to the formation of different surfaces: a low dissolution rate of copper and tin will lead to a protective surface allowing the formation of an enriched tin layer associated with the selective dissolution of copper (Type I structure), while at high copper and tin dissolution rates no protective layers are formed (type II structure).

It doesn't matter what type of corrosion mechanism we are talking about, when an artifact is dug out the sudden change in the environment induces an immediate restart of the corrosion process. This is due to the high concentrations of oxygen in air and to the increase of pollutant level in the last decades. Therefore it is imperative to find efficient anticorrosion methods that can be quickly applied to the bronze artifact.

The use of inhibitors is one of the most practical methods to protect metals from corrosion, especially in aggressive media.[7,8] Various types of organic compounds are used to protect metals from corrosion. It is known that nitrogen containing and sulphur containing organic heterocyclic compounds may act as inhibitors for copper dissolution due to chelating action of the heterocyclic molecule and the formation of a barrier on the copper surface .

Only benzotriazole (BTA), a nitrogen based inhibitor, has been widely accepted in the stabilization of copper and copper alloy artifacts. Madsen [11] proposed BTA for archaeological conservation based on the vast research done for industrial purposes. Due to its perceived advantages and satisfactory results, BTA has been the predominant corrosion inhibitor used in the conservation of copper and copper alloys. Recently, another corrosion inhibitor was suggested for copper corrosion inhibition in conservation: 2-amino-5-mercapto- 1,3,4-thiadiazole (AMT) however, AMT has not been accepted generally for use. Corrosion inhibition efficiency was found to be as follows: sulphur-containing > nitrogen-containing > oxygen-containing [15].

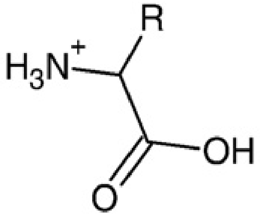
Application of wax mixed with benzotriazole, is the technique often used as a protection method [2,3]. But this technique does not satisfy entirely the ethics of restorers and curators. First, the application of wax changes the surface aspect and second, benzotriazole is known as toxic, and also induces a colour change [2]. Most of the available inhibitors are toxic compounds that should be replaced with new environmentally friendly inhibitors. Literature shows studies of various innoxious compounds that have been studied [9,20]. It was found that 1-(*p*-tolyl)-4-methyl imidazole (TMI), 2-mercapto-5-R-acetylamino-1,3,4-thiadiazole (MAcT) and other several thiadiazole derivatives are efficient and are ready to be used in museums [20]. Despite the vast number of corrosion inhibition investigations, there remains relatively few works directed towards the study of non-toxic organic compounds, especially amino acids, as corrosion inhibitors of Cu [9–11].

Cysteine is a very interesting amino acid that contains, in addition to the amino group the –SH group, which has a strong affinity for copper. Zhang et al. studied the inhibitory action of two amino-acid compounds, alanine and cysteine, on copper corrosion in 0.5M HCl [11]. In the presence of 10^{-5}M of alanine or cysteine, corrosion rates were determined by coupon tests and compared with a conventional benzotriazole inhibitor. Maximum protection efficiency was obtained with cysteine (58.7%) and lower degree of inhibition was recorded with alanine and benzotriazole Polarization curves indicated that the alanine and cysteine acted as an anodic inhibitor. The improved inhibition efficiency of cysteine was attributed to its adsorption on the copper surface via the mercapto group in its molecular structure[20].

The addition of cysteine to the neutral or acidic chloride solution inhibits the corrosion of Cu to a great extent. Results revealed clearly that cysteine is a good cathodic type inhibitor for copper corrosion in neutral and acidic chloride solutions.[Ismail] The mechanism of the corrosion inhibition process is based on the adsorption of the amino acid on the active corrosion sites. Cysteine obeys the Langmuir adsorption isotherm and the calculated free energy of adsorption of cysteine on Cu reveals a strong physical adsorption of the inhibitor on the metal surface.

Baruni [1] tested a set of amino acids such as Arginine (Arg), Cysteine (Cys), Glycine (Gly), Lysine (Lys) and Valine (Val) on the corrosion behaviour of copper in 1 M HNO_3 using weight loss and electrochemical polarization measurements. The inhibition efficiency, as determined from both methods used, was found to vary in the order:

$$\text{Val} < \text{Gly} < \text{Arg} < \text{Lys} < \text{Cys}$$



Literature [1,7,8,11,12] reveals that Cys gives more inhibition efficiency than oter amino acids tested. It is known that the most organic substance employed as corrosion inhibitors can adsorb on the metal surface through heteroatoms such as nitrogen, oxygen, sulphur and phosphorus. Its inhibition efficiency should follows the sequence O<N<S<P [7,8]. The presence of −SH in molecular structure of Cys provokes an increase of the inhibition efficiency. The group −SH is more a donor of electron and it offers itself the possibility to be a center of adsorption beside the atom of nitrogen [9]. In the case of Lys, nitrogen atom in aliphatic chain increases the interaction of molecule with metal surface.

Although Arg has a radical R which contains nitrogen, effectiveness remains low because the existence of a tautomeric and a steric hindrance at nitrogen atoms [2]. The effectiveness of Val and Gly with non-polar hydrocarbon side chain on a carbon is explained perhaps by non-heteroatom on the inhibitor structure.

3. CONCLUSION

The process of corrosion of bronze can be stopped with the use of chemical inhibitors. Several works have been performed on the use of organic compounds as inhibitors for the corrosion of metals in aggressive acidic media. It has been recognized that nitrogen and sulfur-containing organic compounds act as inhibitors for Cu dissolution. Among these organic compounds the most used are benzotriazole [3–5], benzimidazole [6] and tetrazole [7]. Benzotriazole and its derivatives are excellent corrosion inhibitors for copper in a wide variety of water solutions, temperature and
pH ranges, but these compounds are highly toxic

Amino acids were reported as good toxic corrosion inhibitors for many metals in various aggressive media [13–17]. The choice of an inhibitor is generally based not only on the electron cloud of the heteroatom(S, N, Se, O, P). On the other hand, the consideration is also made on the toxicity degree of the tested compounds. Among a set of five aminoacids tested [1] cystein has been proved to be the most efficient corrosion inhibitor for copper.

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