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CORROSION OF BRONZE ART OBJECTS AND METHODS OF RESTORATION

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ABSTRACT

The paper presents a study of the corrosive state of sculptures and art objects made from copper and bronze, the equipment used to detect and study defects and the methods and solutions for restoring the art object surfaces attacked by corrosion

KEYWORD: corrosion, sculptures, art objects, equipment, methods, restoration

1. Introduction

Metal craftsmen in antiquity did not leave a description of the processing methods and composition of alloys used for making various objects. Some notes are available only in the Middle Ages, but the name of alloys and terminology may not always be read, therefore the only sources are the objects that have come up today. From the studies conducted by historians we know that the first objects of copper appeared in VII century till A.C. era. They were forged in native copper. Later, the copper metallurgy and copper alloys with other metals are discovered. For several millennia, different objects have been made from copper such as: work tools, weapons, ornaments and mirrors, dishes, coins (fig. 1), etc.

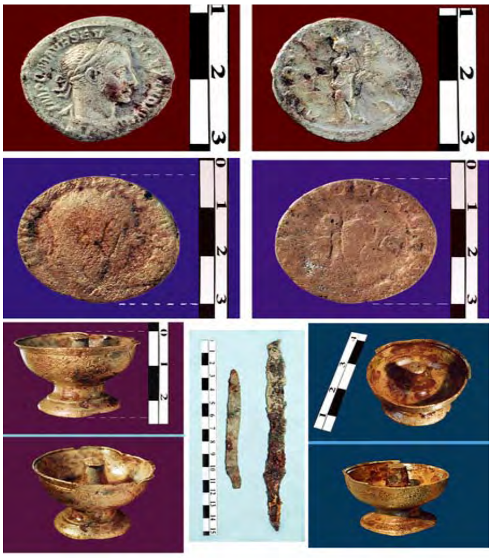

Fig. 1. *Coins, dishes and weapons of bronze*

Ancient alloy compositions are very different, the earliest being those of bronze with tin and arsenic. Besides these components in the ancient alloys there is also lead, zinc, stibiu, iron and others under the form of microimpurities carried away into the metal with the ore.

Alloy composition was chosen rationally according to purpose of the object and the casting technique. Thus for casting objects of art the recipe of the ternary copper-tin-lead alloy that was chosen was used in Ancient Greece, Roman Empire, Middle East, India, China.

On the objects cast in bronze, in time, an oxide film builds up, which in some cases is preserved on the archaeological objects as well [1].

Fig. 2. *Bronze angel from the top of the Alexander's column covered with greenish stain, Sankt-Peterburg.*

2. Experimental researches and results

Copper is chemically poorly active does not change in dry clean air. But the atmosphere we live in contains water vapor and carbon dioxide. Therefore, not incidentally, sculptures made of copper and bronze cover with a tabling greenish patina (fig. 2). In normal atmospheric conditions, the greenish stain/patina is composed of the main copper carbonate (malachite), in the atmosphere with sulfur dioxide (SO2) 3Cu (OH) 2 copper ·objects are covered with the main copper sulfate CuSO4 - 3Cu (OH) 2 and near·the sea - the main chloride CuCl2-3Cu(OH)$_2$.

Interesting is that the greenish patina is formed mostly in the damp air with a humidity of over 75%. Film formation is a self-attenuation process because corrosion products protects the metal surface against the environment. The film formation consists of two stable phases. The first - primary film formation, which is a mixture of oxides and protoxid of pure copper. The duration of this oxidic layer formation - from several months to several years. In time, this layer acquires a brown color, characteristic of copper alloys (fig. 3). In some cases, this layer may darken and become black [2].

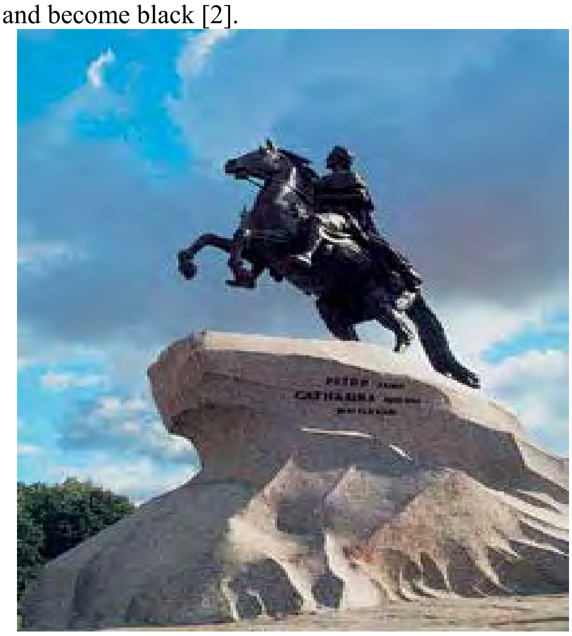

Fig. 3. *Copper horseman, Sankt-Peterburg*

On reaching certain thickness of the oxidic layer, a layer of green copper salts begins to form at the surface. The most likely chemical combinations, formed on copper as a result of corrosion, are the natural minerals. The color (composition and structure of the corrosive layer) depends on the presence in air of various gases, solid particles of different substances, etc. and the composition of the copper alloy. The stain color depends not only on the duration of interaction with the atmosphere and its composition, but also on the composition of the metal, the quality of processing, namely internal and external factors. All atmospheric stains contain oxides and salts. The copper oxide - black color, the protoxide – reddish brown (fig. 4).

Fig. 4. *Monument of Russian fabulist I.A. of Králové from the summer park opened in 1855. Sculptor P.K. Klodt*

The color and shades of green, blue and bluish are given to the patina by the different copper minerals: sulphates - roshantit, antlerit, sulphates in the form of crystalhydrates with a variable content of crystallized water, which are intermediate products in the patina formation; copper carbonates; malachit (Cu2 (CO3) (OH) 2) and azurit (Cu3 (CO3) 2 (OH) 2), nitrates, chlorides in the form of atacamit, paratacamit (Cu2Cl (OH) 3) and botallachit; sometimes the age stain contains copper chloride and copper perchloric crystalhydrate. Practically all the copper oxides and salts, forming the so-called age stain, are insoluble in water, non higroscopic, neutral with respect to copper metal, except for the copper chloride, which means that patina is a natural protection or decorating film.

The natural formation of the age stain on the copper surface stops the corrosion mechanism [3].

Here it is important not to alter the chemical formation mechanism because otherwise a reverse effect may occur.

The thick forged plates of 3-6 mm, used by ancient craftsmen for roof constructions, feature high resistance to atmospheric corrosion. It is worth mentioning, in this respect, the roof of the Hildeshaime cathedral (Lower Saxony, Germany), which survived for 700 years (fig. 5).

A special case of destruction of the copper alloy is the corrosion relapse also called the bronze disease, which may appear on the archaeological objects made from copper and its alloys well as on objects in the museum regardless if they have been cleaned or not. The first signs of disease are characteristic spots occurring on the surface of the object, of light green color and loose structure.

Fig. 5. *Hildeshaime cathedral (Lower Saxony, Germany), which does not need roof replacement for 700 years.*

In the bronze disease outbreak drops of moisture are formed, as these corrosion products are hygroscopic. Gradually these outbreaks extend, covering larger surfaces, attacking the metal profoundly, forming hollows filled with the loose friable substance. After removing the corrosion products, the surface area remains heavily attacked, showing pitting and pits. Destruction may occur at fairly high speed, so that a thin object may be damaged in a few months. There are two causes for such destruction. Firstly, the high humidity and, secondly, the presence of corrosion activators on the metal surface [4]. One of the most dangerous activators is – chloride $Cu + Cl_2 = CuCl_2$.

The chloride can reach the surface of the metallic objects with dust, on a faulty cleaning, by dirty hands touching, from an impure environment, etc.

Corrosion initiators may also be the remains of the formation mass which were not removed from the inner cavities of the art object. Corrosion recurrence develops if the piece is subjected to acid vapors which form with copper different combinations, for example, acetic acid, which is given off from the wood of the museum displays or cabinets or boxes from the warehouse where art objects are stored. It is known the case of a bronze disease occurrences – the Egyptian metal from the Museum in Cambridge, described by the famous scientist in corrosion-Y.R. Evans, who developed a special method for this restoration case.

During the war, after evacuation, objects were transported in green wooden boxes.

The acetic acids vapor, removed from the wet wood, through defects caused by patina, the alloy reacts with copper to form soluble copper acetate, which in turn is transformed, under the action of air oxygen, into base carbonate.

The acetic acid thus formed in the reaction reacts again with the metal and thus it may result in the complete destruction of the object [5]. To study the defects occurring on the surface of the art objects use was made of various devices such as the single device MONOGIL MT 350/6 with roentgen-ray and high-power directed beam, intended for carrying out radiographic research on large thickness, metal, ceramic and stone statues and objects (fig. 6).

Fig. 6 *Portable monoblock type MONOGIL MT 350 / 6 of roentgen ray for research of art objects made of metal, ceramic and stone. Sankt-Peterburg*

On the latest restoration of the sculptural group "the horse tamers" after testing with roentgen rays (fig. 6)it has been established that the entire surface of the four sculptural groups is affected by the bronze disease with caverns depth of 0.35 - 0.5 mm.

Fig. 7. *Rider radiography, China, Tsin dynasty (618-906).*

Fig. 8. *The defectoscop type RDG 500 to control the layer state of preservation, thickness measurement, detection of hidden defects in metal, ceramic and marble sculptures.*

Figure 7 presents the x-ray of a sculptures of the Tsin dynasty, which confirms the integrity of the material: it can be noted the oxide layers and the good piece-casting quality, low density of the material of feet and some parts of the horse saddle.

To control the state of the preservation layer, thickness measurement, detection of hidden defects in metal, ceramic and marble sculpture a defects meters, type GDR 500 (fig. 8) is used. Fig. 8 shows how to conduct research ultrasound researches on the bronze sculpture "Gryphon" in order to determine wall thickness and detect casting defects. The ultrasonic device for measuring thickness type DG 40 B (fig. 9) is used for the detection and measurement of metallic and nonmetallic materials, thickness measurement and study of corrosion in metal sculptures and objects.

Fig. 9 *The ultrasonic DG 40 B.*

After detecting all affected areas measures to restore the sculptures and objects of copper and its alloys are taken. In general, to remove corrosion products use the electrolytic and electrochemical methods are applied. The electrolytic method is used mainly for small objects of art. For large sculptures, of course, the chemical cleaning of areas is resorted to. Works begin with operations of surface preparation, namely, degreasing, cleaning and pickling. Degreasing the surface of copper is accomplished after its polishing or rubbing, until complete removal of traces of corrosive attack and other foreign deposits. By degreasing the oil films and finger traces are removing from the object surface. To do this use is made of various chemical solutions of reagents (table 1).

Table 1

No	Reagents	Cant., g/l
1.	Sodium hydroxide	35
	Anhydrous sodium carbonate	60
	Sodium triphosphate	15
	Preparate OP-7 (or OP-10)	5
Solution temperature – 60 … 70° C Time of processing – 10 … 20 min		
2.	Sodium hydroxide (potasium)	75
	Liquid glass (Na_2SiO_3 or K_2SiO_3)	20
Solution temperature – 80 … 90° C Time of processing – 40 … 60 min		
3.	Liquid glass (Na_2SiO_3 or K_2SiO_3)	10…20
	Sodium triphosphate	100
Solution temperature – 65 … 80° C Time of processing – 10 … 60 min		
4.	Liquid glass (Na_2SiO_3 sau K_2SiO_3)	5…10
	Anhydrous sodium carbonate	20…25
	Preparate OP-7 (sau OP-10)	5…10
Solution temperature – 60…70° C Time of processing – 5…10 min		
5.	Sodium triphosphate	80…100
Solution temperature – 80…90° C Time of processing – 30…40 min		

The chemical cleaning is used when there is no hope to keep the decorative layer of oxide in stable condition. There are many recipes for chemical cleaning. Some are designed for the cleaning of specific objects, proceeding from their specific status, others are universal. A restorer rarely uses universally known methods. It is very important to feel the particular chemical interaction with metal compositions in different states. The general condition with the cleaning chemical is continuously monitoring the process of removing the corrosion products, as the subject can not be left long in solution without being monitored [6]. For chemical cleaning different solutions are used such as: solutions Trilon B (Russia), Versen (USA), Sequestron (England), Titriplex (Germany), Chelaton (Czech Republic) - phosphate acid Disodium *etilendiamintetraacetic* (it is the most common solution to remove products corrosion and deposition of hard soluble calcium, used to restore bronze objects); basic salt solution Seignette or Rachall salt (tartrate of potassium-sodium); *hexametafosfat* sodium - *metaphosphatic* salt acid, *sulphamic* acid, etc. Pickling allows for removal of various corrosion products and impurities from the surfaces of bronze objects. To do this the following solutions are used table 2.

Table 2

No.	Reagents	quant., g/l
1.	Sulfuric acid	25 … 40
	Chromium trioxide	150 … 200
Solution temperature – 25° C Processing time – 5 … 10 min		
2.	Sulfuric acid	150
	Dicromat potassium	50
Solution temperature – 25 … 35° C Processing time – 5 … 15 min		
3.	Soluţie „Trilon B”	100
Solution temperature – 18 … 25° C Processing time – 5 … 15 min		
4.	Chromium trioxide	350
	Sodium chloride	50
Solution temperature – 18 … 25° C Processing time – 5 … 15 min		

After all the preparation steps, the cleaned surfaces shall be subject to patina procedures because they are characterized by specific gloss, and natural patina builds up in time. Depending on the natural color (patina) of the art object use is made of various oxidizing solutions to get the color of the area uniform (table 3).

Table 3

No.	Reagents and color conferred	quant g/l
green		
1.	Ammonium chloride	30
	Acetic acid 5%	15
	copper acetate salt	5
Solution temperature – 25 … 40° C		
2.	Ammonium chloride	16
	Hidrogenooxalat potassium	4
	Acetic acid 5%	1
Solution temperature – 25 … 60° C		
3.	Copper nitrate	10
	Ammonium chloride	10
	Zinc Chloride	10

Solution temperature – 18 … 25° C		
Greenish-yellow		
1.	Copper nitrate	200
	Sodium chloride	20
Solution temperature – 25° C		
From blue to greenish-yellow		
1.	Ammonium carbonate	250
	Ammonium chloride	250
Solution temperature – 18 … 25°		
Old patina look		
1.	Mixture of poly sulphides	25
	25% ammonia solution	10
Solution temperature – 18 … 25° C		

Fig.10. *Angel face on Alexander column before and after restoration. Sankt-Peterburg*

Fig. 11. *Sculpture from group „Horse tamers" before and after restoration. Sankt-Peterburg.*

Figures 10 and 11 present the sculptures "*Angel on the column of Alexander*" and "*Horse tamers*" before and after restoration.

3. Conclusion

- Copper is chemically poorly active does not change in dry clean air. But the atmosphere we live in contains water vapor and carbon dioxide. Greenish patina is formed mostly in the damp air with a humidity of over 75%.

- The stain color depends not only on the duration of interaction with the atmosphere and its composition, but also on the composition of the metal, the quality of processing, namely internal and external factors. All atmospheric stains contain oxides and salts. The copper oxide - black color, the protoxide – reddish brown.

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