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THE HIDDEN SECRETS OF COPPER ALLOY ARTIFACTS IN THE ATHENIAN AGORA

Alice Boccia Paterakis

Abstract

Four copper corrosion products on copper alloy objects in the Athenian Agora collection were analyzed by X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy-Energy Dispersive Analysis Xray (SEM-EDAX), and Ion Chromatography (IC) at the British Museum. Blue/green corrosion was identified as sodium copper carbonate acetate, white crystals as sodium acetate trihydrate, a turquoise blue corrosion as copper (II) hydroxide spertinite, and a dark brown corrosion as cassiterite and cuprite. The factors which may have led to the development of these compounds are discussed which include cleaning and stabilization agents such as sodium hydroxide and sodium sesquicarbonate, and acetic acid from wooden storage materials. The influence the equilibrium Relative Humidity (egRH) of these compounds may have on continued deterioration leads to a consideration of methods for their removal.

1. Introduction

In 1998 blue/green corrosion on copper alloy objects was tentatively identified as a compound based on copper acetate by X-ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR) analysis (1). The XRD patterns of five samples were published for comparative purposes (1).

Further analysis of this blue/green corrosion and other corrosion products has been carried out by XRD, FTIR, Ion Chromatography (IC) and Scanning Electron Microscopy with Energy Dispersive Analysis X-ray (SEM-EDAX) at the British Museum. Thickett had identified a pale blue corrosion product on bronzes in the British Museum as sodium copper acetate carbonate (2,3,4). It has been determined that the build-up of acetic (ethanoic) acid emissions in wooden storage cupboards is a major contributor to the formation of this compound. The objects analyzed from the collections of the Agora and the British Museum had been stored in wooden cupboards since the 1930s. The acetic acid concentration in these wooden cupboards in the British Museum and Agora Excavations has been measured. A concentration of 1267 **µ**gm (500 ppb) acetic acid found in the Agora Excavations is comparable to the levels found at the British Museum: 1071 to 2880 **µ**gm^{-3} (1,2). Relative Humidity (RH) has been shown to play an important role in the corrosive activity of volatile acetic acid on metal (5). In the Agora Excavations the blue/green corrosion was found on a small percentage of the bronze collection and only on chemically stripped objects whereas in the British Museum it was found also on objects which retained their original corrosion products. In the Athenian Agora dark brown corrosion is often found on the surface of chemically stripped objects with the blue/green corrosion (1). It was hypothesized in 199$ that this dark brown corrosion might be copper (II) sulphide covelite or copper (I) sulphide chalcocite resulting from residual sulphuric acid from cleaning. Another explanation offered was the artificial patination of these chemically stripped objects with hydrogen sulphide followed by ammonia or acetic acid vapors (6). Other chemicals published for artificial patination consist of sodium sulphite or sodium thiosulphate solution (7) and sodium carbonate or bicarbonate (8).

White crystals are frequently found interspersed with the blue/green corrosion. It has been observed that these crystals develop after the formation of the blue or blue/green corrosion (8). Thickett and Tennent have identified these white crystals on objects in the British Museum and other collections as sodium acetate trihydrate (2,8). These crystals may take the form of needles or powder. Powder-like white crystals were present on those Agora objects sampled for blue/green corrosion.

2. Analysis

There was insufficient corrosion remaining from the objects analyzed in 1998 for further analysis so six other objects were selected from the Agora collection. Three objects were sampled for the blue/green corrosion, one for dark brown corrosion, and one for a turquoise blue corrosion. These were analyzed by XRD, FTIR, IC and SEM-EDAX at the British Museum.

2.1. Analytical Techniques

XRD samples the spacings between planes of atoms in a crystalline solid. The unique arrangement of atoms in a material generates a unique XRD pattern that can be used for identification. The use of a Debbye Schering camera allows analysis of samples as small as 1 microgram. Analysis was undertaken using Cu (alpha) radiation produced from an x-ray tube operating at 40KeV and 40mA.

FTIR samples the vibrational transitions of a material and can be used for amorphous as well as crystalline materials. Absorption patterns are unique and characteristic. The use of a beam condenser and diamond cell allows analysis of similar sample sizes to XRD. A Spectratech Sample plan diamond cell with a 4x beam condenser on a Nicolet Avatar 360 FAIR was used. The spectra were processed and searched using Nicolet Omnic ESP software and libraries developed by the British Museum and in collaboration with the Infra-Red Users' Group. A combination of both XRD and FAIR can be very powerful and allow a full identification to be made.

IC is a modification of liquid chromatography and can allow simultaneous determination of many anions and cations in solution including acetate. Analysis was undertaken with a Dionex DX300 system using an AS12A column with 2.7mM sodium carbonate and 0.3mM sodium hydrogen carbonate eluent for anions and a CS12 column with 20mM methane disulphonic acid eluent for cations.

SEM-EDAX can generate elemental analysis from extremely small samples (1 micron diameter). It can be sensitive and quantitative for all elements except boron and hydrogen. A Joel 840 SEM with Link analyzer system was used for this work.

2.1.2. Samples Analyzed from Copper Alloy Objects

#1 blue/green corrosion from unidentified object found in 1936 in a cistern
#2 blue/green corrosion from handle of a bucket found in 1937 in a well
#3 blue/green corrosion from unidentified object found in 1939 from mixed fill
#4 turquoise blue corrosion from bowl found in 1932, object completely mineralized
#5 dark brown corrosion from unidentified object found in 1939

Objects # 1, 2, 3 and #5 had been chemically stripped. It is not known what chemicals or methods were used to strip these objects although zinc and sodium hydroxide for electrochemical reduction are likely candidates. Object #4 was completely mineralized preserving the original corrosion products of cuprite and malachite. Although object #4 has not been chemically stripped it could have been treated with sodium sesquicarbonate. Dark brown corrosion and white crystals coexist with the blue/green corrosion on objects # 1, 2, and 3 in relatively small quantities. The blue/green corrosion and dark brown corrosion consist of a soft powder which was easily removed from the surface. The pale blue corrosion of object #4 is intimately bound to the surface of a layer of malachite, which rests on cuprite. It was removed with a scalpel attached to the malachite layer.

3. Results of Analysis

The blue/green corrosion (samples # 1, 2, and 3) has been identified as sodium copper acetate carbonate ($NaCu(CO_3)(CH_3COO)$, the same compound found on copper alloy objects in the British Museum (2,3,4). SEM-EDAX detected sodium copper carbon and oxygen as the major elements present. IC of a dilute sulphuric acid solution determined the presence of both acetate and sodium ions (copper and carbonate would not be detected with the instrument configuration used). The presence of carbonate was confirmed by effervescence with acid. The sodium copper acetate carbonate on Object #2 was found to be insoluble in water as was this compound in the British Museum (3). Sodium acetate trihydrate ($CH_3COONa.3H_2O$) was found on Object #2 which may reflect an abundance of white crystals in this sample (3,8). Both FTIR and XRD are insensitive to less than 5-10% of a material within a mixture. Sodium acetate trihydrate was confirmed with XRD and FTIR. Sodium acetate and sodium acetate trihydrate are water soluble (9). The turquoise blue corrosion (sample #4) has been identified as copper (II) hydroxide spertinite [($Cu(OH)_2$]. This compound was indicated by SEM-EDAX and confirmed by XRD. The dark brown corrosion (sample #5) is mainly tin oxide, cassiterite (SnO_2), and copper oxide, cuprite (Cu_2O), with a trace of zinc. SEM-EDAX indicated mainly tin and copper with some oxygen and carbon and a trace of zinc. XRD confirmed cassiterite and cuprite.

4. Discussion

4.1. Blue/green Corrosion

The contribution of acetic acid emissions from wooden storage cupboards undoubtedly plays a major role in the formation of sodium copper acetate carbonate (samples 1,2,3). Acetic acid concentration, temperature and relative humidity are important factors in the formation of copper acetates on bronze objects and the higher these levels the greater the possibility. The concentration of acetic acid may have been much higher when the storage cases were new and it should be kept in mind that the objects have had up to 60 years in which to develop the acetate corrosion product. The RH in the Agora storeroom was monitored over a one year period and was found to reach a maximum RH of 82% in the winter months. Also, the buffering capacity of the wooden cupboards should not be discounted in the consideration of RH inside the cases. The sodium copper acetate carbonate found in the British Museum was observed to deliquesce at a RH of approximately 65% and the equilibrium Relative Humidity (eqRH) of sodium acetate trihydrate was found to be 75% (3).

Other sources of acetate could be vinyl acetate and polyvinyl acetate adhesives, lacquers and consolidants which were used in the 1940s, 1950s and 1960s (1). Perhaps the small percentage of objects which have developed the sodium copper acetate carbonate represent those treated with acetate-based polymers.

Sodium which contributed to the formation of sodium copper carbonate acetate in the Agora may derive from 1) the burial environment, 2) chemical cleaning agents such as Calgon (sodium hexametaphosphate), zinc and sodium hydroxide, alkaline Rochelle salt (5% sodium hydroxide and 15% sodium potassium tartrate), alkaline glycerol (15% sodium hydroxide and 40% glycerin), and 3) the stabilization compound sodium sesquicarbonate. Conservation treatment records of individual objects were not kept in the early years of the excavation.

One possible explanation for the formation of sodium copper acetate carbonate may be found in the use of sodium sesquicarbonate. The formation of cuprite, tenorite and sodium copper carbonate hydrate (chalconatronite) on copper alloys which have been treated with sodium carbonate or sodium sesquicarbonate is a well documented fact (10,11,12,13). The copper corrosion products are dissolved and the copper salts are redeposited as small crystals of sodium copper carbonate hydrate. Perhaps the sodium copper acetate carbonate found on some of the Agora and British Museum objects consisted initially of sodium copper carbonate hydrate which over the years in wooden cupboards took up acetic acid forming sodium copper acetate carbonate.

Another explanation for the formation of sodium copper acetate carbonate could be the incomplete reduction of the secondary copper corrosion products such as malachite during the electrochemical cleaning. Any remaining malachite would serve as a host for the formation of sodium copper acetate carbonate. Assuming that the majority of chemically stripped objects were completely reduced this would explain why only a small percentage of these artifacts in the Agora Excavation have developed the blue/green sodium copper acetate carbonate. Thickett has shown that the presence of sodium is necessary for the formation of sodium copper acetate carbonate (3). Most likely two factors are required: the incomplete reduction of copper carbonates and residual sodium from incomplete rinsing after cleaning. The formation of sodium copper acetate carbonate does not seem to be dependent on alloy type (3).

4.2. Turquoise Blue Corrosion

The turquoise blue corrosion (sample #4) was identified as copper (II) hydroxide spertinite, $Cu(OH)_2$. The spertinite was found to be insoluble in water as reported (9). This compound is duck-egg blue, unstable in the presence of carbon dioxide and water, and poorly crystalline (12). In the presence of carbon dioxide it has a tendency to change into copper hydroxy carbonates or, in the presence of chloride, into copper hydroxy chlorides (atacamite, paratacamite) (15). Under normal ambient conditions copper (I) hydroxide it will undergo dehydration forming cuprite (Cu_2O). If there is a significant amount of moisture present, i.e. in the pores of hygroscopic corrosion products on corroded bronze, the dehydration process will be minimized thereby stabilizing the copper hydroxide. A high ambient RH may contribute to the moisture present in the corrosion products. In addition to the significant presence of water two other factors may support its stability: 1) the localized pH and 2) the presence of a mixture of tin (II) and tin (IV) corrosion products on the surface and the presence of degraded metal underneath. MacLeod has found many hydroxy species associated with tin hydrolysis (15). An additional factor which may stabilize the copper hydroxide is the adsorption of SO_2. Only one other instance of copper hydroxide on a copper alloy object has been found in the literature and that was from a marine context (14).

The use of sodium sesquicarbonate on this object cannot be ruled out although sodium was not detected in the analysis. It is possible that copper (II) chlorides and copper hydroxy chlorides, formed from the oxidation of copper (I) chlorides in the corrosion matrix, could be hydrolized by sodium sesquicarbonate (depending on the hydroxide concentration in solution) forming copper (II) hydroxide (15). The fact that sodium and acetate were not detected on this object, which had been stored in the same conditions as the other objects, substantiates the theory that the presence of residual sodium may be necessary for the formation of compounds based on copper acetate in wooden cases (3).

4.3. Dark Brown Corrosion

Cassiterite (SnO_2) and cuprite (Cu_2O) were found to make up the dark brown corrosion (sample #5). The primary tin and copper corrosion products present in the original corrosion front would have been exposed by the removal of the secondary corrosion products on the surface during cleaning. The primary oxidation product of tin, Sn2+, is subjected to hydrolysis and can be precipitated or the tin (II) can be further oxidized to tin (IV) which can then undergo hydrolysis. Chemical cleaning of tin and copper corrosion products, and the removal of copper (I) chloride complexes (e.g. with sodium sesquicarbonate), results in the hydrolysis of soluble tin (IV) and copper (I) materials producing cassiterite and cuprite. In electrochemical reduction with zinc and sodium hydroxide any non-reduced secondary copper corrosion products, such as malachite, form cuprite (Cu_2O) and tenorite (CuO), which appear as a black, powdery corrosion (12). The tin corrosion products, which generally are not reduced to tin metal, would be hydrolized to produce cassiterite (15). The trace of zinc detected by SEM-EDAX may be a residue from the zinc and sodium hydroxide electrochemical reduction method.

While the dark brown corrosion and blue/green corrosion occur together they seem to form independently from one another. The only common factor in their formation appears to be sodium, for example from sodium sesquicarbonate, which could have contributed to the formation of cuprite from copper (I) chloride in the dark brown corrosion (12) and the sodium copper acetate carbonate (blue/green corrosion).

5. Conclusion

The possibility of ongoing corrosion caused by the deliquescence of the sodium copper acetate carbonate and the sodium acetate trihydrate should not be overlooked. If RH levels cannot be maintained below the eqRH of these salt compounds then the removal of these corrosion products should be considered. Their removal could be carried out in the dry, crystalline state by mechanical means or in the liquid, deliquescent state by rinsing with an appropriate solvent or by absorption into a poultice.

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