Analysis of Bronze Disease Treatments
By Scanning Electron Microscopy.

Nicole Bishop*, Brian Pauley

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Executive Summary

Bronze disease is a type of self-progressing corrosion of bronze. This degradation is thought to be caused by humidity but proliferated through the formation of chlorine containing compounds further reacting with the air. The damage that this corrosion can cause can destroy priceless artifacts. It is important that possible “cures” are determined and that their effectiveness is assured in order to save these artifacts from degrading to a pile of green powder. Scanning electron microscopy can show the effects of treatments of bronze disease on a small scale. This method will allow for a minimally destructive case study in the effectiveness of some common treatments for bronze disease to be tested.

Introduction

Corrosion of bronze artifacts, given the name “bronze disease” is a major opponent in the fight to preserve the bronze artifacts to be appreciated generations later. This bronze disease manifests itself as a green powder, or as a thick hard coating on the surface of an artifact. This is not to be confused with patina which is the green or brown film caused by oxidation over long periods of time. The patina will not cause degradation of the artifact as the bronze disease will but the bronze disease begins within the patina due to the chloride containing compounds within this layer\(^1\). There is conflict regarding what exactly the chemical composition of the bronze corrosion is, some of the theories include; cuprous chloride\(^2,3,6\), copper trihydroxychloride compounds\(^4,6\), and nantokite\(^5\) among others. There are others who state that there have been multiple kinds of bronze corrosion on the same artifact including combinations of the chemical constituents noted previously but interestingly eventually containing malachite, a copper carbonate hydroxide mineral\(^6\). In order to preserve these artifacts from further degradation a method must be formulated to remove the current corrosion. Bronze disease is thought to arise from being kept in humid conditions, above 35% humidity\(^3\) however once the degradation has begun it can continue through a series of self-sustaining degradative reactions\(^7-9\). These reactions do eventually stop stabilizing the artifact but not before unrepairable damage has been done. It follows that if the artifacts are going to be preserved it is best to remove the source of the bronze disease in order to prevent the cascade of chemical reactions that further damage the piece.

There are a variety of proposed methods to remove bronze disease at the source, the copper and chlorine compounds. These treatments include; soaking the sampled portion of the artifact in a solution of sodium sesquicarbonate\(^2,3,5,10\), soaking in a solution of benzotriazole\(^2,3,4,7,10\), soaking in a solution of 5-amino-2-mercapto-1,3,4-thiadiazole\(^3\), and the application of zinc dust\(^11\). Many of these methods were tested in their effectiveness through visual observations. This project would study the treatments on a much smaller level. Does this treatment remove the copper and chlorine compounds causing the bronze disease and what does this treatment leave behind?

Most of the artifacts proposed for use in this project have another interesting trait that ties all of them together, they all are experiencing the beginning of their bronze degradation at the interface between the metal and a leather piece on the artifact. This is likely due to the organic acids in the chemical treatments of the leather\(^12\).
Technical Approach

The instrument that will be used is the scanning electron microscope that also does energy dispersive x-ray analysis (SEM/EDX). The SEM can show details regarding the surface topography and thus show differences in the amount of corrosion on the surface. The EDX will elaborate on the topographical map by overlaying on the surface where certain elements are located. Both analyses can be done simultaneously due to the fact that both detectors, for the SEM and for the EDX, are reading different kinds of data. The SEM is reading for back scattered electrons originating from the electron gun, low energy secondary electrons being blasted from the surface of the sample as a result of impact of an incident electron, and high energy auger electrons which are being ejected from an atom via x-ray emission. EDX is detecting characteristic x-rays to allow certain elements in the sample to be detected and mapped spatially over the topographical map of the surface. Figure 1 shows a visual depiction of the types of signals created from the electron gun and which portion of the instrument use that data in its analysis.

![Diagram showing the types of signals created from the electron gun.](image)

Scanning Electron Microscopy (SEM)

Scanning electron microscopes work by looking at reflected electrons similar to how a compound microscopes look at reflected light through a series of lenses. The biggest difference between these two techniques is the resolvable distance achievable with each technique. Compound microscopes are limited by the visible range of light the shortest wavelength is 400 nm therefore a compound microscope can only resolve down to 200 nm\(^{13}\). A scanning electron microscope is not limited by visible light and uses electrons instead, providing a resolvable distance of 8 nm with a magnification of 50,000x\(^{14}\). The data that is taken from the SEM looks like the data in figure 2. Raised edges appear light whereas deeper more “shadowed” portions are darker.
Energy Dispersive X-Ray Analysis (EDX)

The EDX works through the emission of characteristic x-rays for certain elements these x-rays result from the collapse of electrons into lower shells when a hole is created from the ejection of a secondary electron. This collapse fluoresces with x-rays and can also eject an auger electron. This interaction is depicted in figure 3.

The wavelength of the x-rays that are emitted are specific to the atom in which they originated in and thus can be used to map an element's abundance across the surface of the sample as shown in figure 4.
Fig. 4 Example data that can be collected with the EDX the brighter portions of the map show where the element is distributed within the sample. In this example this sample has large amount of Mn and no Fe.

Fig. 5 Diagram depicting the instrumental setup of the SEM/EDX including the electron gun, the focusing lenses and the electron detectors of the SEM as well as the X-ray detector of the EDX.

The SEM/EDX consists of an electron gun that passes through a set of condensing lenses that direct the electrons into parallel lines. The entire testing chamber is placed under vacuum to prevent electron interactions with the air. The parallel beams of electrons then pass through multiple magnetic lenses, which direct the incident electrons until they are focused on a small area. This beam is passed through a scanning coil which controls the rate that the scan is completed as well adjusting the energy of the incident electrons. This electron beam is directed at the sample and scans over an adjustable surface area. The sample is affixed to the sampling platform via a piece of carbon tape, which absorbs electrons, to provide a blank background to work on. There are two independent types of detectors in the instrument. Two electron detectors, one to detect the backscattered electrons, and one to detect secondary electrons.
There is also an x-ray detector for detecting characteristic x-rays of desired elements for relative spatial abundancies\textsuperscript{15}.

**Proposed Research**

Four possible bronze disease treatments will be tested; sodium sesquicarbonate, benzotriazole, 5-amino-2-mercapto-1,3,4-thiadiazole, and zinc dust. The success of the treatment will be determined by comparing the treated SEM data with the original SEM data taken by Brian Pauley. He will be characterizing the degradation of the sampled bronze prior to treatment with one of the 4 treatments. We will be looking for a change in the locality or amount of trace chlorine as well as anything new that can be seen on the SEM for what the treatment leaves behind. 3 SEM pictures will be taken of each sample; the untreated corrosion, the corroded area after an initial scraping is completed, the area after the chemical treatment has been applied. This will allow for the assurance that the change seen on the artifact is due to the treatment and not as a result of the scraping of the corroded pieces.

Sample preparation for the SEM/EDX is done as follows; a corroded portion of the sample (less than half of a square centimeter) is removed from the artifact and attached to a sample holder using a portion of carbon tape. The sample is then be loaded into the SEM and placed under vacuum. The crude X,Y, and Z dials are used to orientate the sample, and the magnification and focal controls are adjusted on the computer program.

This data is important for determine the effectiveness of the proposed bronze disease treatment because the SEM can show the topography of the sample which allows for a visual cue as to whether bulk corrosion products have been removed. The EDX can show the presence or lack thereof of chlorine compounds this allows for a more quantitative measurement of the effectiveness of the process because the EDX can detect trace amounts of chlorine better than simply by visual detection even at 50,000x magnification.

Due to the semi-destructive nature of this method, a small piece needs to be removed from the artifact for sampling, artifacts that are experiencing more severe damage will be sampled.

**Sodium Sesquicarbonate**

A similar method to Hughes, W. A. (1970)\textsuperscript{10} will be used. A 5% by weight solution of sodium sesquicarbonate (aka Borax substitute) will be created using distilled water, it should be noted that the sodium sesquicarbonate contains roughly 4 ppm sodium chloride. This basic solution will dissolve the copper and chlorine compounds making up the degradation as well as neutralizing the resulting hydrochloric acid. The artifact portion will be allowed to soak for 2 weeks after which the largest amount of the compounds should be dissolved. In most procedures it is noted that this soak should be changed weekly and be continued for multiple months in order to see complete results, 2 weeks should suffice for a decrease in the degradation product to be seen in the SEM. Full removal does not need to be seen to see an improvement in the amount of degraded surface material.
Benzotriazole (BTA)

A similar method to Madsen, H. B. (1967) will be used. After preliminary scrubbing of the artifact it will be cleaned with a 1::1 mix of toluene acetone. The cleaned artifact will be submerged in a 3% by weight solution of BTA in methylated spirits under vacuum. It will be left to soak until no more bubbles emerge from the sample. This method does not recommend multiple treatments, so a change is expected to be visible after the first treatment.

5-Amino-2-mercapto-1,3,4-thiadiazole (AMT)

A similar method to M. C. Ganorkar, V. P. (1988) will be used. 150 mL of a 0.01 M solution of AMT in distilled water will be applied to the metal sample under vacuum. Drops of Nitric Acid will be added and the entire solution will be heated to 60 °C and left to soak for an hour. The sample will be rinsed with distilled water and then repeated for another hour. As with the sodium sesquicarbonate treatment it is suggested to repeat until the bronze disease is completely removed but as before two repetitions of this treatment should be enough to show a decrease in the copper and chlorine compounds to suggest complete remediation with enough repetitions. If no such change is observed the treatment will be repeated another time.

Zinc Dust

A similar method to V.C. Sharma, et. al (1995) will be used. After the preliminary scrubbing of the artifact zinc dust moistened into a paste with ethanol will be applied to the affected areas with a paintbrush and the spot will be moistened with ethanol 10 times per day for 3 days to produce a tough seal of grey reaction products. The purpose of this method is both to create a protective seal to prevent further degradation of the material but it also acts as a patch to replace some of the volume that may have been lost to the degradation.

Conclusions

It is important to determine the effectiveness of the current treatments for bronze disease so that informed decisions can be made about how to best treat artifacts based upon the artifacts characteristics. Should it turn out that none of the above techniques work as expected it may be a sign that more research needs to be done in this area to create an effective treatment. If it does work it may give us a bit more in depth look at the chemical mechanism that is driving both the bronze disease as well as the treatments that work to remove it.
Works Cited


(15) J. Sebree, Personal Correspondence.