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Analysis of corrosion layers in ancient Roman silver coins with high resolution surface spectroscopic techniques

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ABSTRACT

Determination of the microchemistry of surface corrosion layers on ancient silver alloy coins is important both in terms of understanding the nature of archaeological environmental conditions to which these ancient coins were exposed and also to help in their conservation. In this present study, five ancient silver alloy coins (225 BCE–244 CE) were used as test vehicles to measure their immediate surface microchemistry and evaluate the appropriateness and limitations of High Sensitivity-Low Energy Ion Scattering Spectroscopy (HS-LEIS, 0.3 nm depth analysis), High Resolution-X-ray Photoelectron Spectroscopy (HR-XPS, 1–3 nm depth analysis) and High Resolution-Raman Spectroscopy (HR-Raman, ~1000 nm depth analysis). Additional information about the deeper corrosion layers, up to ~300–1000 nm, was provided by dynamic HS-LEIS and HR-Raman spectroscopy. While not archeologically significant, the use of these coins of small commercial value provides data that is more representative of the weaker signals typically obtained from ancient corroded objects, which can be in stark contrast to pristine data often obtained from carefully prepared alloys of known composition. The oldest coins, from 225 to 214 BCE, possessed an outermost surface layer containing Cu_2O, Na, Al, Pb, and adsorbed hydrocarbons, while the more recent coins, from 98 to 244 CE, contained Cu_2O, Ag, N, F, Na, Al, S, Cl, and adsorbed hydrocarbons in similar corresponding surface layers. It thus appears that alloying with copper, even in small amounts, leads to the formation of an outer Cu_2O layer. Depth profiling revealed the presence of K, Na, Cl, and S as key corrosion components for both sets of coins with S, most likely as Ag_2S, concentrated towards the surface while the Cl, most likely as AgCl, penetrated deeper. Schema to understand the overall chemistry of the corrosion layers present on these silver alloy coins were developed from the equipment limitations encountered and are presented.

1. Introduction

1.1. Justification of research

In ancient and medieval times, silver was the normative basis for trade and monetary systems [1] because gold was too elitist for national use. Silver was also the primary metal of choice for elitist decorative objects [2]. The durability of silver is usually enhanced by the addition of alloying elements, with copper being the most common alloying additive. Even a few percent copper in silver significantly increases its hardness and additions of up to 20 wt% are not uncommon (as a point of interest "925" Sterling Silver is nominally 92.5 wt% Ag, 7.5 wt% Cu). At room temperature, the solubility of copper in silver is negligible and, consequently, such silver alloys are present as either non-equilibrium solid solutions or have two-phase microstructures [3]. The archaeological literature is not always clear as to the purity of silver of an object. Depending on the environmental conditions, different silver oxidation species (chloride, sulfide, or oxide) are thermodynamically stable; the nature of the corrosion product is therefore highly dependent upon the corrosion environment [4,5]. Silver has little solubility for oxygen in the bulk lattice but appreciable diffusivity for oxygen along

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grain boundaries [6] making it susceptible to grain boundary corrosion. Silver with copper in solid solution is susceptible to internal oxidation with copper corroding preferentially to form copper compounds [7–9]. The addition of copper has a significant effect on the nature and character of the corrosion layer, but this is not well documented.

The ancient silver coins examined in this current study were, thus, used as test vehicles to investigate the appropriateness of new high resolution capabilities of surface characterization techniques and methods, both destructive and non-destructive, for the study of corrosion on archaeological silver objects. Knowledge of the surface corrosion layers of these ancient silver coins is important both in terms of understanding the nature of archaeological environmental conditions to which these ancient coins were exposed and also to help in their conservation. The coins were chosen from the historical period where the copper content is known to vary widely [10–12], in an attempt to observe how variation in copper content manifests itself in high resolution spectroscopic techniques and affects the microchemistry of the corrosion layers of these ancient silver coins. To the best of the author's knowledge, controlled corrosion studies of either modern or ancient silver-copper alloys relevant to this study do not exist.

A broad array of microchemical analysis techniques have now been developed and applied to the study of cultural heritage objects by both archaeologists and museum conservation scientists. These techniques may be divided into destructive, minimally invasive, and non-destructive methods. The choice of a specific approach is situational, depending on many factors such as philosophy, ethics, politics, sacredness, economics and emotional consideration [13]. Thus it is common to use ancient coins as test vehicles because they are often found in large quantities, and are often of low value. The destructive analysis of one Roman copper coin in a hoard of 1000 is a considerably different situation to that of a single Greek gold coin of great beauty. While some aspects of the present study involve destructive modification of specimens, this is only meant to focus on limitations of some of the techniques used; the use of non-destructive or minimally invasive methods is always preferred for analysis.

The five coins studied here were obtained on the open market and are unprovenanced. While not archeologically significant, the use of these coins of small commercial value provides data that is more representative of the weaker signals typically obtained from ancient corroded objects, which can be in stark contrast to pristine data often obtained from beautifully prepared alloys of known composition. Residuals due to fingerprints are a possibility arising from open market coins, however, this has been noted only qualitatively in the literature with little focused research other than forensic applications having been performed [14].

2. Materials and methods

2.1. Coins

The five coins studied here were obtained on the open market. These unprovenanced coins were chosen mainly because of their representative range of copper composition rather than their specific archaeological significance. Similarly, although both ancient and modern forgeries of Roman coins are known, they are rare, and are not considered [10]. The silver content of the coins is estimated to be: Jupiter-Quadriga (225–214 BC, ~97–99 wt%), Trajan (98–117 CE, ~85 wt%), Caracalla (198–217 CE, ~55–60 wt%), and Gordian III (225–244 CE, ~45 wt%). Another coin with known high silver composition, Phoenicia (Tyre, 5/6 CE, ~97–99 wt%), was also included in this study [12]. The coins were not cleaned previous to any experiment reported here, but a few Raman spectroscopy experiments involved heating and surface modification. A few Raman spectroscopy experiments (not shown for brevity) and a XPS experiment were performed on the coins after a fresh fracture, but the results were the same as untreated samples.

2.2. Raman spectroscopy of the coins under ambient and *in situ* controlled environments

The Raman spectra of the coin corrosion layers were obtained with a high resolution, dispersive Raman spectrometer system (Horiba LabRam-HR) equipped with three laser excitations (532, 442, and 325 nm). The lasers were focused on the samples with a confocal microscope equipped with a 50X long working distance objective (Olympus BX-30- LWD, numerical aperture = 0.50) for the visible. Ambient Raman spectra were collected with the 532 nm laser at 2 cm^{-1} resolution with an accumulation of 5 scans at 5 s/scan with a 200 μm laser hole size to minimize the focal plane depth (providing more surface sensitive information). The instrument is calibrated using a Si standard at 520.7 cm^{-1} before spectra are collected.

For *in situ* dehydrated Raman measurements, a fractured piece of coin was placed in an environmentally controlled high-temperature reactor (Harrick High-Temperature Reaction Chamber) containing a quartz window. The sample temperature was controlled by a Harrick ATC Temperature Controller unit (ATC-024-4). The protocol for obtaining *in situ* Raman spectra under a slightly oxidizing environment was performed as follows. To dehydrate the sample, the coin was initially heated at a rate of 10 °C/min in the *in situ* Harrick cell to 400 °C and held for 10mins under 30 mL/min of either flowing inert Argon (Airgas UHP Argon gas) or 1% O_2/Ar (Mix of: Airgas 10% O_2/Ar and Airgas UHP Argon gas). The sample was allowed to cool naturally to room temperature (RT) after the dehydration, but remained under the slightly oxidizing environment. The Raman spectra were collected with the 532 nm laser at 400 °C and also at RT after thermal treatment with an accumulation of 3 scans at 30 s/scan and a 200 μm laser hole size. After the thermal treatment, several spots on the coin were examined for corrosion homogeneity Unless noted, all Raman spectra shown are from room temperature collections.

2.3. High resolution-X-ray photoelectron spectroscopy (HR-XPS)

HR-XPS was performed using Lehigh University's Scienta ESCA-300HR-XPS spectrometer system utilizing a 300 mm hemispherical electrostatic analyzer and monochromatic Al Kα X-rays with energy of 1486.6 eV generated from a rotating anode and monochromator. The detector is a Photonis Chevron dual multichannel plate assembly. The Ag 3d 5/2 Full Width at Half Maximum (FWHM) is 0.44 eV at 368.30 eV. Each spectrum was calibrated using a binding energy (BE) value of 285.0 eV for carbon in the C1s region. Charge compensation (using a low energy electron flood gun aimed in the direction of the sample) was used for the analyzed coins. The atomic concentration ratios were calculated by correcting the measured peak area ratios with relative sensitivity factors employed in Casa XPS software version 2.3.15.

A freshly fractured piece of the Caracalla coin was transferred to the UHV chamber (~10^{-8}–10^{-9} torr) for analysis. A survey spectrum was initially performed to analyze elements in the outer corrosion layers. A 1.6 mm line profile was performed across the fracture coin surface, beginning at the corrosion edge and scanning toward the center of the coin. The survey spectrum was performed with 2 scans at a pass energy of 300 eV. The line profile spectra were performed in 0.1 mm steps with 4 scans each at a pass energy of 300 eV. The line scan was directly imaged onto the detector using an electrostatic lens.