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Complementary analytical methods for analysis of Ag-plated cultural heritage objects☆

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ABSTRACT

In a preliminary study of American silver-plated cultural heritage objects with the Dallas Museum of Art (DMA), variable plating thickness was observed, which complicates non-destructive characterization of the base metal. Therefore, the objective of this study is to compare the effectiveness of three non-destructive complementary analytical methods to characterize both the plating and the base metal of a typical Ag-plated object and to contrast these results with conventional destructive metallographic methods. An externally purchased 20th century sacrificial Ag-plated "Century" fork was chosen for this study and is similar to one found in the DMA's collection. First conventional destructive metallographic methods, where cross-sections were taken and then characterized using optical microscopy (OM) and scanning electron microscope (SEM) with energy dispersive X-ray spectroscopy (EDS), were employed in order to evaluate the effectiveness of the non-destructive methods. The first non-destructive method, synchrotron radiation X-ray diffraction (SR-XRD), reveals the plating thickness, texture related to processing methods, and the phases present in both the base metal and the plating. The second method, dual beam focused ion beam (FIB)/(SEM) equipped with an (EDS) system, provides elemental composition of both the plating and the base metal, as well as imaging of the plating thickness and grain structure, giving some insight into processing methods. The last non-destructive method, handheld X-ray fluorescence (XRF) spectroscopy, provides qualitative elemental compositions of both the plating and the base metal. Each non-destructive analytical method yields complementary results about the composition, plating thickness, texture, and phases present in the plating and base metal of the Ag-plated "Century" fork and aids in the verification of the results from the other methods. Through these methods, we show that successful characterization of Ag-plated cultural heritage objects is possible non-destructively, thus maintaining the object's structural, historical and artistic integrity.

1. Introduction

In general, scientific studies of historical and cultural objects are focused on determining the provenance, condition, and manufacturing technologies of the people who produced them [1–4]. The analytical examination of silver and silver-plated cultural heritage objects is no exception [5–8]. Most of the past and present scientific studies of these silver or silver-plated objects, deal with the examination of coins [9–22], or jewelry [23] from ancient and medieval cultures. Although some studies have been performed on more modern silver alloy objects [24–28], there still exist a void for the study and characterization of electroplated silver objects from the Modernist movement of the late 19th and early 20th Century.

It is the author's intent to fill this void by performing a systematic study of the Jewel Stern American Silver Collection at the Dallas Museum of Art (DMA) which contains over 400 Ag and Ag-plate objects from the Modernist movement of the late 19th and early 20th Centuries. These objects have been well-documented historically in *Modernism in American Silver* [29], but there is still a need for a comprehensive technical study of these materials to gain better insight into the craftsmen and industrial manufacturers of these objects and the time period. This information can provide valuable information to conservators, historians, and current industrial manufacturers. Furthermore, the base metal compositions and processing are not well-documented for most of the objects in the DMA collection; however, evidence of changes in composition and processing have been periodically released by the manufacturers, e.g. through advertisements.

One of the major challenges with studying ancient and modern cultural heritage objects is that they must be non-destructively and non-invasively examined, which often requires a combination of analytical techniques for full or even partial characterization [30–35]. Analytical techniques, such as conventional laboratory X-ray diffraction (XRD) and X-ray fluorescence (XRF) allow for surface studies of the objects which are extremely beneficial for the study of corrosion products and surface treatments, but cannot properly examine the base material

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without prior knowledge of the underlying structure; furthermore, these surface studies can be misleading with respect to the base metal and difficult to interpret since many objects have alterations on the surface layers such as corrosion, tarnishes, patinas, plating, and post-excavation cleaning residues [36–39]. For example, Mass et al. [28] calculated an emission depth of 20.3 μm for the Cu Kα line through a pure Ag matrix, the case for silver alloys with an enriched surface layer or silver-plated copper, meaning that copper becomes almost undetectable in small quantities once plating depths reach greater than 20 μm. It should also be noted that both XRD and XRF can now be performed *in situ* using portable devices and both have become common practices in the analytical study of cultural heritage objects [40–46]. Studies on the base material can be performed non-destructively using synchrotron, neutron, and proton sources available at large user facilities due to their much greater penetration depths; however, it is difficult to examine large bodies of work due to the nature of these facilities [47–51].

In this paper, it is the aim to compare and contrast three complementary "non-destructive" analytical techniques used in cultural heritage studies: 1) high energy (transmission mode) synchrotron radiation X-ray diffraction (SR-XRD), 2) focused ion beam (FIB)/scanning electron microscopy (SEM) milling, and 3) handheld XRF spectroscopy, on a sacrificial Ag-plated object from the Modernist movement, similar to an object in the DMA's collection but purchased for destructive examination, to determine an effective way to characterize both the plating and the base metal. These results are then compared with conventional destructive metallography to validate the non-destructive methods. This comparison is then used to determine an effective method to reliably and quickly characterize Ag-plated objects from the American Modernist movement. In addition, it can be easily seen how the combination of these methods can be readily applied to many other questions in cultural heritage studies where a thick surface alteration, greater than 5 μm, is in an integral part of the piece as a whole.

2. Methods

The object chosen for this study, Fig. 1, is a sacrificial 20th Century International Silver Co. fork that was made for the Seaboard Airline (SAL) Railroad train system, referred to from here on as the "Century" fork. The "Century" fork measures $1.9 \times 2.5 \times 19.1$ cm^3. The "Century" fork is from the same manufacturer and line with the "Century" pattern as the "Century" flatware set (for the New York Central System's 20th-Century Limited train system) in the DMA's collection. In addition the "Century" flatware sets were intentionally plated with a thick silver layer to withstand heavy use by passengers while still maintaining their polished appearance. By selecting an object with a thicker Ag-plating it is now possible to explore the limits of each non-destructive technique. SR-XRD patterns were taken at the Advanced Photon Source (APS) in Argonne National Labs using transmission mode at a beam energy of 70 keV, beam size of 50×200 μm^2 and exposure time of 2 s per frame. 2-D diffraction patterns was analyzed using Fit2D and a custom Matlab code provided by the beam line scientist at the APS. Non-destructive FIB/SEM was performed using an FEI Nova Nanolab 200 equipped with an EDAX energy dispersive X-ray spectroscopy system (EDS) according to the procedure outlined in Carl et al. [52], which follows the basic steps: 1) mount an object to the stage such that it can avoid contact with all parts of the microscope during tilting, 2) select a region of interest and tilt specimen 52° from normal to align ion column perpendicular to the surface, 3) deposit a thin layer of Pt (~1–5 μm) to protect cross-section and avoid "curtaining" effect, 4) mill a rectangular pattern into surface to reveal a cross-section perpendicular to the surface of the object, and 5) clean the cross-sectional face using a low current ion beam. XRF spectra were collected with a Bruker Tracer-III SD handheld XRF spectrometer using 304.8 μm Al and 25.4 μm Ti filters at 40 keV and 30 μA to optimize detection of transition metals. All spectra were collected over a live time of 120 s. Artax software was used to fit the peak area of the Zn K_α and K_β peaks for thickness approximations. Conventional destructive metallography was performed after non-destructive testing by cutting cross-sections from the fork and hot mounting them in a conductive graphite mold. Microstructure of the cross-sections was revealed using a solution of HNO_3:H_2O at a 1:1 ratio. Optical micrographs were taken using a Zeiss Axio Lab.A1 microscope in bright field and captured using an Axiocam 105 color camera. Further microstructural and elemental characterization was performed using the same FEI Nova Nanolab 200 system as describe above. In order to check the accuracy of the EDS quantification method, two standard samples with known compositions as determined by manufacturer's supplied inductively coupled plasma–optical emission spectroscopy (ICP-OES) data and a third sample which was closer in composition to our actual object but the manufacturer did not supply ICP-OES data and only supplied the targeted composition. The results are shown in Table 1.

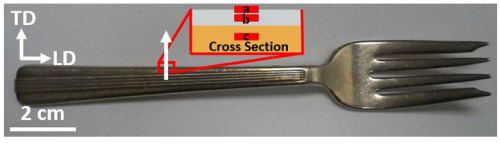

Fig. 1. 20th Century International Silver Co. fork from the Seaboard Airline Railroad train system with a "Century" pattern showing transverse (TD) and longitudinal direction (LD). The arrow shows the motion of the "Century" fork for SR-XRD for positions a, b, and c in Fig. 2.

3. Results and discussion

3.1. Synchrotron X-ray diffraction

Fig. 1 illustrates the motion of the fork during diffraction measurements. Diffraction patterns were taken in 10 μm steps as the fork was moved into the beam, thus generating different patterns with respect to position across the sample in order to isolate the plating layer from the base metal as much as possible. The boxes labeled a, b, and c in the schematic in Fig. 1 correlate to the approximate beam position of the representative Debye–Scherrer diffraction rings shown in Fig. 2a–c, respectively. One quarter of a Debye–Scherrer diffraction ring from 110 to 120 μm from the edge of the "Century" fork, which contains both the plating and the base metal, is shown in Fig. 3. The plating material consists of pure FCC Ag, while the base metal consists of an FCC Cu–Zn–Ni solid solution alloy. Close examination of the rings show slight texturing in both the plating and the base metal most likely associated with residual strain due to rolling of the base metal and/or an anneal to homogenize the grain structures after rolling and plating. The normalized 1-D integrated diffraction patterns are presented in Fig. 4 as a function of distance from the edge of the "Century" fork. It is clear that only two distinct macroscopic layers exist, an approximately 40–50 μm thick Ag-plating and a FCC Cu–Zn–Ni solid solution alloy base metal. The lattice parameters were calculated to be 4.09 Å and 3.65 Å for the plating and base metal, respectively. The plating lattice parameter is in good agreement with the literature value for pure FCC Ag [53]. Using Vegard's law, $a_{A_{(1-\chi)}B_\chi} = (1-\chi)a_A + \chi a_B$ [54], and historical

Table 1
Manufacturer wt.% composition data vs. measured EDS quantification.

	C510 bronze		C360 brass		C770 nickel silver	
	OES	EDS-SEM	OES	EDS-SEM	Aimed	EDS-SEM
Cu	95.19	95.6 (0.2)	61	64.5 (0.1)	55	54.3 (0.3)
Sn	4.6	4.4 (0.2)	–	–	–	–
P	0.1	–	–	–	–	–
Fe	<0.01	–	0.041	–	–	–
Pb	<0.005	–	2.501	1.5 (0.1)	–	–
Ni	<0.05	–	–	–	18	18.2 (0.2)
Zn	0.04	–	36.458	34.0 (0.1)	27	27.4 (0.4)