Scanning Electron Microscope and Focused-Ion Beam Analysis of Corrosion Sites on Lead-Tin Alloys

CNF Project # 1346-05
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Abstract:
Focused ion beam (FIB) was used to cut micron-scale cross-sections through corrosion crusts on acetic-acid corroded lead-tin alloys. The exposed surfaces were mapped chemically using SEM/EDX. The results of the mapping provide insight into the role of tin content in susceptibility of these alloys to organic acid attack.

Summary:
Lead-tin alloys are the most common materials used to construct organ pipes, both in instruments built today and in those remaining from past centuries. Corrosion of these pipes is widely observed, eventually leading to cracks and holes that rob the pipes of their ability to produce sound. Especially for irreplaceable historic instruments, this corrosion is of great concern, and research is needed to determine its causes and mechanisms.

For very lead-rich (> 99% Pb) alloys, organic acids have been found to be a major cause of corrosion [1]. The acetic acid emanating from the wood of organ cases is likely to be a source of damage in lead-rich pipes. Our research has as its goal understanding how the susceptibility to acetic acid attack changes as a function of alloy composition. We carried out laboratory exposure experiments in which lead-tin alloy coupons were exposed to low, controlled concentrations of acetic acid vapor. Alloys with tin contents ranging from 1-10% were studied. We used grazing incidence angle x-ray diffraction to identify the bulk corrosion products that formed on the sample surfaces, but we needed more detailed analytical methods that would allow us to characterize the morphology of corrosion products and to resolve chemical information at corrosion sites.

Using the Zeiss Supra SEM at CNF, we obtained images of sample surfaces at magnifications ranging from 100x-4000x. The low-mag images revealed that the surfaces are not covered with uniform corrosion layers but that corrosion crusts with dimensions of 10-100 µm are interspersed among areas with thin oxide coverage. At high magnification, it was possible to see the individual 1-2 µm crystallites making up the thick crust areas.

Next, we used the FEI 611 FIB to cut cross sections of 10-20 µm through corrosion crusts. Compared with traditional sectioning and polishing, this is a gentler method of preparing cross-sections for SEM analysis. The gallium ion beam does not cause mechanical damage to the corrosion crust or the underlying bulk metal, and by following removal of significant material with a high beam current (2000 pA) with a polishing step at lower beam current (500-1000 pA), it was possible to minimize impregnation of the surface with gallium.

Each cross-section was cut at a 45° angle with respect to the surface normal, creating a surface that is horizontal when the sample itself is tilted at 45° in a microscope. In this orientation, SEM/EDX (using the Zeiss Supra) or SEM/WDS (using the JEOL microscope located in Snee Hall at Cornell) was used to map lead, tin, and oxygen content in the oxide crust and underlying metal. For each alloy, tin was segregated along the oxide-metal interface, allowing us to hypothesize that it has a barrier role in the corrosion process. Current work is being directed at using similar cross-sectional analysis to track evolution of this segregated layer with time and under atmospheres of varying humidity.

References:
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Figure 1, top left: Lead-tin alloys were exposed to low concentrations of acetic acid, simulating the conditions that lead to deterioration of lead-tin alloy organ pipes. This micrograph shows a surface with discrete corrosion crusts separated by areas of thin oxide coating.

Figure 2, bottom left: A FIB cross-section cut at 45° to the surface normal can be studied with SEM/EDX.

Figure 3, above: An image of the cross-section shows the oxide layer and bulk metal, containing tin inclusions.

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