Oral presentation

Shedding light into metal corrosion on Tang dynasty gilded bronzes using 3D Electron Diffraction

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The in-depth understanding of manufacturing technique and corrosion process of cultural heritage materials very often requires reliable structural characterization. Techniques like X-ray diffraction, Scanning Electron Microscopy, Raman, Fourier Transformed Infrared Spectroscopy are usually employed to the study such materials. In recent years, scientific community has also shown a renewed interest using Transmission Electron Microscopy based characterization methods, which provide structural details at nm scale using very small quantities of material. In particular, we have shown how 3D Electron Diffraction (3D ED) and Phase & Orientation mapping in TEM (ASTAR technique) can be applied for the study of nanocrystalline phases present in Greek amphorisks, Roman glass tesserae, Chinese Bronze artifacts of the Shang Dynasty (from British Museum collections) and several Maya pigments [1, 2].

As a part of the continuing work, we have recently investigated headgear metal consisting of bronze type Cu-based core which has been gilded by a thin gold layer. The sample comes from a newly excavated female tomb in Xi’an of the Tang dynasty tomb (618-907 CE). Optical Microscopy imaging and SEM EDX analysis shows that the samples consist of thin gold layer (about 400 nm) with Cu rich layer (~ 50-100 micron) on the top of the gold layer and then the final surface oxide layer (main composition of Cu and O) having needle shaped crystals with length few tens of microns. The goal of the investigation is to understand the alloying process and detailed analysis of the corrosion product. For the TEM experiment three different thin beam transparent lamellas (~ 4 x10 micron) of different layers of the material was prepared using Focused Ion Beam (FIB) from a larger fragment (~ 15 x 15 x 0.35 mm) of the sample. Initial 3D ED study was performed on the surface oxide layer and the thin gold layer of the prepared lamella. In 3D ED, a small nanocrystalline grain is selected with beam size of ~100 nm with certain convergence angle and tilted in the range of -60° to +60° with a step size of 1°. The sample tilt was combined with beam precession of 1° for reducing dynamical effect and improving integration of reflection intensities. 3D ED analysis on several individual phases with a needle morphology revealed the unit cell is very close to the structure of malachite mineral $Cu_2CO_3(OH)_2$ with monoclinic unit cell a= 9.5 Å, b= 11.97 Å, c= 3.24 Å, β = 98.75° [Fig. 1].

3D ED has also been applied to study the gold layer. It appears that the gold layer consists of very small domains of overlapping nano crystals with size less than 50 nm. From the collected 3D ED, some of the 2D ED patterns were indexed as cubic Au (a=b=c= 4.07 Å), whereas diffraction patterns with overlapping spots are possibly arising from more complex nano structures.

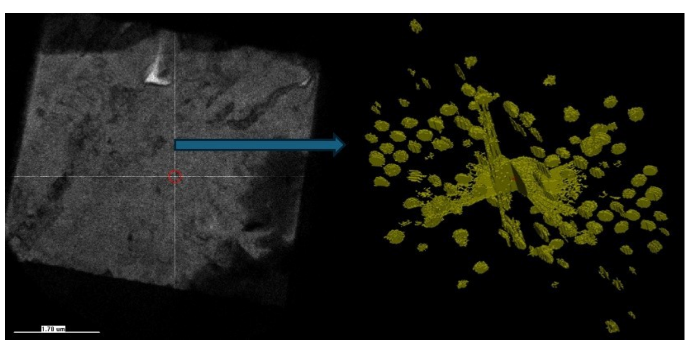

Figure 1. 3D diffraction data (right) collected from a single nanocrystal from the corrosion oxide layer (left)

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