High-energy synchrotron X-ray diffraction and imaging of ancient Chinese bronzes

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Introduction

Two bronze objects in the ancient Chinese art collection of the Art Institute of Chicago (AIC) were investigated using noninvasive, high-energy x-rays (85 keV): a bronze fragment from an early Western Zhou dynasty vessel (*Hu*, $11^{th}/10^{th}$ century B.C.) and a bronze dagger-axe (*Ge*, $3^{rd}/2^{nd}$ century B.C.) with a silver-inlaid sheath. Results were compared with compositional results obtained by traditional techniques [1,2] and with laboratory x-ray images [3]. Both objects are several millimeters thick, highly leaded bronzes and, thus, are difficult to penetrate and study with low-energy x-rays.

Experimental Methods

All experiments were performed at the 1-ID beam line of the APS. A monochromatic x-ray beam (λ= 0.015 nm; 85 keV) with cross-section variable between 20 x 200 μm^2 and 200 x 200 μm^2 was employed for the experiments, with exposure times of approximately 60 seconds. The setup for diffraction and phase-contrast, edge-enhanced imaging has been described in detail in Refs. [3-4]. The images obtained were compared with traditional x-ray images, recorded at the AIC using a Philips radiographic system operating between 100-320 KV.

Results and Discussion

The bronze fragment was composed of three phases: a Cu-rich phase consisting of face-centered Cu with up to 16 wt % Sn in solid solution, an intermetaillic Sn-rich phase with $Cu_{41}Sn_{11}$ composition (33 wt.% Sn), and a nearly pure Pb phase as seen here and previously reported in Refs. [1-3]. Spatially resolved synchrotron x-ray diffraction at one edge of the fragment was performed, mapping the phases present with 20 µm steps from the outside corner down to 1.3 mm. The diffraction patterns collected at each discrete step within the bronze fragment – positioned with its vertical face at a 30° angle relative to the beam – show a transition from a thin patina of cuprite (Cu_2O) and cassiterite (SnO_2) at the surface (Figure 1) to an intermediate, partially mineralized (corroded) zone to the uncorroded bulk metal (Cu, $Cu_{41}Sn_{11}$ and Pb) which was previously observed destructively [1,2]. Diffraction patterns also indicate that the oxide phases (corrosion products) are fine grained, while the three metallic phases are coarse grained, thus confirming that the vessel was produced by casting rather than by cold- or hot-working. The bronze dagger-axe (Fig. 2a) was determined to have been cast as a single piece consistent with a purely ceremonial function rather than to conceal a functional interior blade. Superior to traditional x-ray radiography (Fig.2b), phase-contrast, edge-enhanced synchrotron x-ray imaging (Fig.2c) reveals extremely sharp detail and improved contrast at the same magnification including the intricate shape of the silver inlay. Large dendrites in the imaging and large diffraction spots (i.e. large grain size) in the diffraction patterns indicate slow-cooling rather than subsequent hot- or cold forming. An extensive series of synchrotron radiographic images also supported that no blade is present within the sheath. The fine-grained silver inlay was mechanically applied onto the bronze object (likely by hammering) after casting.

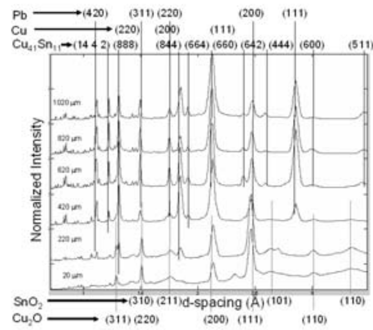

Figure 1. Selected diffraction patterns for bronze fragment at six different 200 µm step-depths from fragment corner.

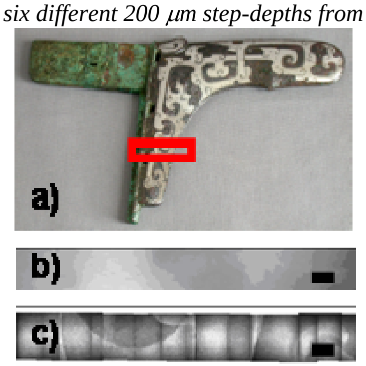

Fig. 2: a) Bronze dagger-axe (20 x 13 cm). Photo Courtesy of AIC, Conservation Department; b) traditional x-ray radiograph of mid-section of dagger-axe highlighted in a) with the red box (the bar measures 1 mm); c) a mosaic of synchrotron x-ray images of same mid-section of dagger-axe

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