SYNCHROTRON APPLICATIONS IN ARCHAEOMETALLURGY:
ANALYSIS OF HIGH ZINC BRASS ASTROLABES

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ABSTRACT

Synchrotron X-rays were used to perform non-destructive transmission diffraction and fluorescence experiments on a group of 24 European and Islamic astrolabes dated between 1350-1720 A.D. in order to determine their compositions. A group of six astrolabes produced in Lahore between 1601-1662 A.D. were found to contain a mixed $\alpha + \beta$ brass microstructure, proving that the brass was produced by a co-melting technique rather than the traditional cementation process. The results also show evidence of dezincification, attributed to heavy annealing of the brass during astrolabe manufacture. This effect was so severe that accurate analysis of the bulk Zn composition could not be determined from the fluorescence results alone; transmission X-ray diffraction gives a more accurate measurement of the bulk Zn composition.

INTRODUCTION

The planispheric astrolabe (Figure 1) was the most sophisticated instrument of pre-telescopic astronomy, its use dating from approximately 700 AD to the mid 19th Century AD in Islamic Lands and from 1000 AD to mid 17th Century in Europe. The astrolabe could be used as a timepiece both during the day and night, depending on whether the sun or the night stars were visible. Astrolabes were also used as a surveying tool to measure distances for accurate maps, as well as for astronomical calculations [2]. However, such a valuable tool was not constructed easily and was often ornately decorated to illustrate an instrument maker’s skill. The finest materials available were used (predominantly brass), and the instrument’s accuracy was determined by the quality and uniformity of the degree markings with which master engravers finished the astrolabes. It is for these reasons that astrolabes were treasured at their time of manufacture and in current day as scientific instruments and works of art. Due to their rarity and value as art, completely non-destructive analysis techniques are required to study the metallurgy of the astrolabes.

In this study, a group of 24 European and Islamic brass astrolabes from the Adler Planetarium and Astronomy Museum in Chicago, IL, has been examined by non-destructive synchrotron X-ray methods to determine alloy composition. These methods include X-ray transmission diffraction and X-ray fluorescence to determine surface and bulk composition as well as the metallurgical phases present in the microstructure. In this paper we explain why it is sometimes necessary to use both X-ray diffraction and fluorescence to obtain accurate chemical compositions for valuable historic artifacts that require non-destructive analysis techniques.
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EXPERIMENTAL PROCEDURE

A variety of non-destructive techniques based on synchrotron-produced X-rays were used to measure the composition of the astrolabe alloys. Synchrotron X-rays have many advantages over standard lab source X-rays. The desired X-ray energy can be selected (ranging from 10-100 keV) with small energy spread (approximately 100 eV). Synchrotron X-rays also have very high brilliance, approximately eight orders of magnitude greater than a standard lab source. These characteristics allow experiments to be performed which previously were impossible. These techniques and their benefit to the current study include:

1) X-ray Transmission Diffraction Experiments – The metallurgical phases present in the bulk microstructure were determined by peak location in transmission X-ray diffraction. This allows the examination of the interior of the astrolabe without the sampling associated with traditional metallography. The $\alpha$ phase brass Zn composition was determined from the location of the (111) $\alpha$ brass diffraction peaks and by using Vegard’s Law [3] [4].

2) X-ray Fluorescence Analysis – The near surface composition of the sample, to a depth of approximately 10-20 $\mu$m, can be obtained by measuring the secondary X-rays generated by the impinging X-ray beam [5]. This was performed to determine alloy composition used for each astrolabe component, and by comparison with the Zn composition measured by diffraction to determine if dezincification has occurred. Fluorescence analysis also allows for examination of all trace elements present in the astrolabes.

The astrolabes were taken to beamline 1-ID-C at the Advanced Photon Source synchrotron at Argonne National Laboratories in Argonne, IL, for synchrotron analysis. The X-ray beam conditions for the synchrotron experiments were 100 x 100 $\mu$m beam size, and 71 keV beam energy. To ensure that the astrolabes would not be harmed, a sample of modern brass of similar composition was exposed to the X-ray beam for many hours to examine for possible surface tarnishing. None was found, ensuring that the astrolabes to be examined (which would only see
exposure to the X-ray beam for a time of only a few seconds) would not be harmed during examination.

RESULTS AND DISCUSSION

Zn compositions of the brass astrolabes determined by the diffraction and fluorescence techniques are shown in Figure 2. The initially expected result was that the data points would fall on the indicated 1:1 fit line. This is true up to a limit (represented by the gray band in Figure 2), which is the phase boundary between the α and α+β regions (approximately 0-36 wt% Zn) as seen in Figure 3. This is represented by a gray band instead of a line due to the temperature dependence on the boundary location indicated in Figure 3. Vegard’s Law states that the lattice parameter of a single phase binary alloy will vary linearly with the amount of alloying element added [4]. Data from Pearson verifies this to be accurate for the Cu-Zn binary system [3]. For all Zn concentrations above 36 wt%, the lattice parameter of the α brass does not change (only the relative amount of α and β phases change and Vegard’s Law cannot be used to determine the bulk Zn concentration). This is still a valuable fact because the presence of β phase in the microstructure is a clue to the manufacturing process used to create the brass.

In pre-modern history, the most common process to form brass was by the cementation process [7, 8]. Originally perfected by the Romans for the minting of brass coinage, the process involves heating zinc oxide in the presence of both charcoal and metallic copper to approximately 1000 °C. The zinc oxide is reduced to zinc vapor (zinc boils at 906 °C) and carbon dioxide; this zinc vapor then diffuses into the metallic copper (which does not melt until 1083 °C) to form brass. This process was used in Europe until the early 19th century, when efficient and clean techniques to produce metallic zinc were perfected [9]. A practical limitation of the cementation process is that the maximum zinc composition is approximately 32 wt% Zn due to the thermodynamics of the reaction [10]. Thus, any historical brass with a zinc composition significantly higher than...
this 32 wt% barrier must have been produced by another technique (which will be discussed later).

![Cu-Zn Phase Diagram](image)

Figure 3 – Cu-Zn phase diagram [6]

Figure 2 also shows a few points (encircled) with a significant decrease in the fluorescence Zn composition relative to the diffraction composition. This is attributed to dezincification; a surface depletion of zinc as a result of annealing. The astrolabe components illustrating this discrepancy are all sheet-formed components, which would have been annealed at least once during forming. The volatility of the zinc would cause the zinc near the surface to diffuse into the zinc-free atmosphere of the annealing furnace, causing the outmost few microns of the component to have a lower zinc composition than the bulk. This is a very important point to emphasize, as most non-destructive compositional analysis of historic artifacts is performed by X-ray fluorescence. Therefore, if the data is reported without knowing the forming history of the artifact, it could be a misleadingly low zinc composition. Prior to using synchrotron X-rays, the only way to determine this compositional difference was through destructive metallography. These dezincified components were only a small subset of the sheet formed astrolabe components, so it may be that this was not an intentional result by the maker. It is possible that this dezincification effect could be the basis for the lack of existing evidence of high zinc brasses for the period 13th -17th Century in the Indian continent.

The diffraction results for all of the European astrolabes (Figure 4) showed $\alpha$ brass and metallic lead phases, consistent with brass manufactured by the cementation process in use at the time of astrolabe manufacture (1532-1600 A.D. for the astrolabes in this study). The metallic lead is a tramp element from the zinc ore [11], and it precipitates out as globules between the brass grains due to low Pb solubility. However, in a number of the Islamic astrolabes originating from the Lahore region of current day Pakistan, there was $\beta$ as well as $\alpha$ brass and metallic lead in the alloy (Figure 5). This means that the brass compositions must be between 39-45 wt% Zn, which...
could only have been manufactured by co-melting of metallic zinc and copper. The Lahore astrolabes, dated from 1603-1660 A.D., therefore predate European co-melting brass technology by approximately 200 years [9]. It has been shown that metallic zinc had been refined in the region since the 13th century; however it has only been speculated that this zinc was used for brass production [12].

Figure 4 - Diffraction pattern for 1532 A.D. astrolabe manufactured by Georg Hartmann (illustrated in Figure 1) illustrating $\alpha$, and Pb phase peaks.

Figure 5 – Diffraction pattern for 1662 A.D. astrolabe manufactured by Diya al-Din Muhammad in Lahore illustrating $\alpha$, $\beta$, and Pb phase peaks.

CONCLUSIONS

By using high brilliance synchrotron X-rays it is possible to perform transmission X-ray diffraction experiments to obtain metallurgical data without the need to cut and polish a metallographic sample. Thus, synchrotron study provides a completely non-destructive approach to the study of ancient metal artifacts. This method has been applied to a study group of 24 historical astrolabes from Europe and Islamic Lands ranging from North Africa to current-day Pakistan. The data has shown that the European astrolabes are representative of traditional brass manufacture and forming techniques, while the Islamic astrolabes centered in Lahore display a much more advanced brass manufacturing technology. These high zinc Lahore astrolabes also indicate evidence of a long annealing cycle during fabrication resulting in a dezincification layer near the surface. The use of synchrotron techniques has pointed out a potential problem with using standard XRF for non-destructive chemical analysis: use of XRF alone can result in a misleadingly lower zinc composition due to the nature of this near surface measurement technique.
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