Neutron diffraction study of Levantine Middle Bronze Age cast axes

El’ad N. Caspi¹, Sariel Shalev²,³, Sana Shilstein³, Anna M. Paradowska⁴, Winfried Kockelmann⁴, Yossi Levy⁵

¹Physics Department, Nuclear Research Centre – Negev, POBox 9001, 84190 Beer-Sheva, Israel
²Leon Recanati Institute for Maritime Studies & Institute of Archaeology, University of Haifa, Mount Carmel, 31905 Haifa, Israel
³Kimmel Center for Archaeological Sciences, Weizmann Institute of Science, 76100, Rehovot, Israel
⁴Rutherford Appleton Laboratory, ISIS Facility, Chilton Didcot, Oxfordshire OX11 0QX, UK
⁵Israel Antiquity Authority, PO Box 586, Jerusalem 91004, Israel.

E-mail: caspie@nrcn.org.il

Abstract. A neutron diffraction study on 6 Middle Bronze Age axes, cast from tin bronze or from arsenical copper, has been carried out using the ENGIN-X beamline at ISIS. The gauge volumes dimensions were 4x4x10mm³; data were collected along the lengths of the objects in their central parts, as well as on the blades, in order to establish the spatial phase contents. Average phase fractions were determined by Rietveld analysis. The main phases identified were solid solutions, corrosion phases and metallic Pb inclusions. We have observed distributions of lattice constants of the solid solutions Cu–Sn, and Cu-As inside each gauge volume in the central parts of the axes due to segregation, or liquation effects. However, the Cu-Sn variations were significantly less pronounced in comparison with typical inhomogeneity effects in as cast objects. The results indicate that the studied Middle Bronze Age axes were probably treated at high temperatures for homogenization necessary for generating sufficient hardness, especially on the blades.

1. Introduction

Socket axes in duckbill- or chisel-shapes were found in “Warrior tombs” of the Middle Bronze Age (about 2000 years b.c.) in Rishon LeZion, Israel. These axes were produced by casting of tin bronze or arsenical copper containing lead. The Sn content (up to about 14%) or As content (up to 5%) is important for improving the mechanical properties of an axe in comparison with a pure Cu axe. Some amount of Pb (up to 2–3%) is applied to improve liquidity of a molten metal during the casting process. Usually, some spatial variation of the doping metals (Sn, As, and Pb) has been observed in such cast tools. In many ancient objects variation in spatial distribution of both doping metals (Sn, and Pb, or As, and Pb) had been established, using mainly XRF. In some cases, the local Pb concentration...
was found to be 20% [1]. Since the effective depth of an XRF analysis in copper alloys is in the order of tens of micrometers, it is important to verify that the above mentioned spatial distribution is in fact a bulk property. Additionally, investigation of the existence (or non-existence) of Sn, or As inhomogeneities, typical for cast objects is of great interest as indication of the metal working. The importance of studying archaeological artefacts using bulk methods was demonstrated in our previous work, where neutron diffraction (ND) method for ancient artifacts had been used [2,3]. In this research, a pilot ND study was carried out on 6 Middle Bronze Age axes using ENGIN-X at ISIS.

2. Samples and experimental set up
ND analyses were conducted on six artefacts obtained from the Antiquity Authority of Israel (Fig. 1): one tin bronze duckbill-shaped axe BA8 (A-2731/97, L.743, B.7327); three tin bronze chisel-shaped axes BA3 (A-2502/96, L.506, B.5077), BA6 (A-2731/97, L.654, B.6362), and BA10 (A-2731/98, L.1075, B.6727); two arsenical copper axes BA12 (A-2731/98, L.1118, B.9418), and BA16 (A-2731/98, L.755, B.7844). Only the BA3 axe was in a virgin corroded state. All other axes were cleaned mechanically and treated for conservation.

Diffraction measurements on ENGIN-X [4] were carried out with gauge volumes of 4x4x10mm$^3$. Measurements were performed along the lengths of the objects in their central parts, and also on the blades. The analyses were carried out to establish the phase contents (Cu–Sn or Cu–As solid solutions, intermetallic compounds of Cu, and Sn or As, Pb metal, corrosion products) and inhomogeneities (segregation) of Cu–Sn or Cu–As solid solutions.

![Fig. 1 – The axes on the ENGIN-X sample holder. Left (from top to bottom): BA8, BA12, BA16, right (from top to bottom): BA10, BA3, BA6. Note for scaling that the chisel-shaped axe BA16 is 165 mm long and that the chisel-shaped axe BA10 is 102 mm long. The dotted line on BA8 exemplifies the ND line scan.](image)

Data (d-range between 1.25 Å – 2.9 Å) were analyzed in detail using the Rietveld refinement method with the GSAS (EXPGUI) code [5,6]. The refined model contained between 16 and 22 variables including phases weight fraction values, cell parameters (with starting values taken from the corresponding literature [7-10]), background, and scale factors. For peak-shape modeling we used the time-of-flight function #3 available in the GSAS code ([5], and references therein), usually used for ENGIN-X data analysis, by refining only $\sigma_1$ for the main solid solution phases. The resulted weighted profile agreement factor values, $R_{wp}$, [5] varied in the range 7-12%.

3. Results and Analysis
The ND patterns of all studied axes show three strong lines associate with the \{111\}, \{200\}, and \{220\} family of reflections (c.f. Fig. 2), belonging to a face centered cubic type lattice. The lattice parameters estimated from these reflections are in the range of 3.66 Å to 3.68 Å in the Sn bronze axes, and in the range of 3.62 Å to 3.63 Å in the As bronze axes. These values are in good agreement with cell parameters values of the $\alpha$-phases, or solid solutions: Cu-Sn (tin bronze) and Cu-As (arsenical
copper), respectively [11,12]. In most of the diffraction patterns, additional small reflections lines are observed associated with impurity phases and corrosion products. These lines are strongest on both edges of the studied axes (close to the edge of the blade, and in the handle). The intensities and positions of the impurity lines are in agreement with the CuCl [7], Cu$_2$O [10], SnO$_2$ [8], and Pb [9] phases for the tin bronze axes. Except for SnO$_2$ the same impurity lines appear in the diffraction patterns of the arsenical copper axes. Neither in the tin bronze axes nor in the arsenical copper axes were secondary intermetallic phases found (e.g. δ-phase in Cu-Sn [11]; or Cu$_6$As, and Cu$_3$As in Cu-As [12].

Close inspection of the diffraction patterns taken from all tin-bronze axes shows significant broadening, or strong peak asymmetry of the copper alloy reflections in the bulk data, collected at a distance from the edges (~20-30 mm from the edges of the blades; henceforth “bulk”) compared to lines in patterns obtained right on the edges. This broadening, or peak asymmetry either increases or retains the same value as a function of the studied gauge volume distance from the blade edge of each of the three chisel shaped axes (BA3, BA6, and BA10). In contrast, for the handle part of the duck-bill shaped axe BA8 (approximately 63 mm from the blade edge, close to “eyes”), the observed line width is similar to the one observed on the edge of the axe.

A detailed Rietveld analysis of all measured diffraction patterns was undertaken. The refined model used consisted of two main phases (solid solutions with different cell parameters), corrosion phases (i.e. Cu$_2$O, CuCl for all tin-bronze and arsenical copper axes, and an additional SnO$_2$ phase for the tin-bronze axes), and a metallic Pb phase. Good agreement between refined model and observed data is achieved for all diffraction patterns ($R_{wp}$ between 7-12%). As an example, the cell parameter values of the two main tin-bronze solid solutions as a function of spatial position, x, along the BA6 axe, are depicted in Fig. 3, alongside with a picture of the studied axe. It is important to emphasize here that the use of the two solid solutions model for the analysis of the ND data is undertaken in order to simplify the data analysis process. The existence of a continuous compositional shift of solid solubility could not be ruled out by the observed data. Nevertheless, the use of this model does not affect our main conclusions.

For BA6 the Rietveld refinement of patterns collected at distances of up to ~30 mm from the blade edge gives a good fit with only one tin-bronze solid solution in the model. At a distance from the blade edge, i.e. in the bulk of the axe, a good refinement requires two different solid solutions (about 60% and 40% in weight), in agreement with the observed lines shape. Moreover, the difference in the cell parameters of the two solid solutions increases as a function of distance (Fig. 3). Similar behavior is also observed in BA3, and BA10, which are all chisel-shaped tin-bronze axes. In the duckbill-shaped axe, BA8, the refinement indicates one solid solution phase close to the blade, with two different solid solutions in the bulk part, and, again, with one solid solution close to the “eyes”. Following the calibration curve published in [11], and using the refined values of the cell parameters associated with
the tin-bronze solid solutions we are able to estimate the tin content in the different parts of the studied axes. The average tin content for all tin-bronze axes is in the range of 7 – 10 wt% for the chisel-shaped axes, and ~11 wt% for the duck-bill-shaped axe. In all tin-bronze axes, the average tin content is constant along the length of the axe. However, the width of the tin distribution, as evidenced by the necessity to use two copper alloy phases, increases from edge to bulk. As an example, the width of the tin distribution of the axe BA6 (Fig. 3) is 5-11 wt% in the bulk, indicating a considerable degree of tin segregation. On the other hand, the sharp tin distribution on the edge indicates that the axe had undergone considerable heat treatment for hardening of blade edge.

![Fig. 3 – BA6 tin-bronze refined cell parameters values as a function of distance from the blade edge, as deduced by Rietveld refinement of the "two phases' model" (see text) to the ENGIN-X data. Error bars values, deduced from the refinement process, are smaller than symbols sizes.](image)

In the diffraction patterns of the arsenical copper BA12 axe no change of the line widths of the main phase is observed as a function of distance from the blade edge. However, the diffraction lines measured for this axe are broader than those from BA16 lines. Moreover, the BA12 peak broadening is even more pronounced than from the edges of the Cu-Sn axes, indicating considerable segregation effects in this arsenic copper axe, even on the edges.

The refined Pb weight fractions show maximal values on the blade edges, but in no case do they exceed ~3 wt% (optimal for casting). It means that the earlier observed high Pb local concentrations (~20 wt%) by XRF [1] are definitely connected with surface effects, probably related to conservation treatments.

In conclusion, we found that neutron diffraction provides additional unique non-destructive information on the internal structure of Bronze Age axes, especially regarding the technology of their production. In particular, the indications in the observed microstructure of heat treatment for mechanical hardening demonstrate rather high qualification of the metal experts nearly 4000 years ago. Moreover, such post-manufacture treatment is a demonstration that the presently studied Middle Bronze Age axes were probably destined for use as weapons, rather than for use as ritual objects.

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