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A non-destructive view with X-rays into the strain state of bronze axes☆

L. Glaser [a,*], A. Rothkirch [a], S. Techert [a], M. Freudenberg [b]

[a] Deutsches Elektronen-Synchrotron, Notkestraße 85, D-22607 Hamburg, Germany
[b] Stiftung Schleswig-Holsteinische Landesmuseen Schloss Gottorf, D-24837 Schleswig, Germany

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ABSTRACT

In this paper we present a new approach using highly surface sensitive X-ray diffraction methods for archaeometrical investigation highlighted on the Neolithic Axe of Ahneby. Applying the $\sin^2\Psi$-method with a scintillation detector and a MAXIM camera setup, both were usually applied for material strain analysis on modern metal fabrics. We can distinguish between different production states of bronze axes: cast, forged and tempered. The method can be applied as a local probe of some 100th of μm^2 or integrative on a square centimeter surface area. We applied established synchrotron radiation based methods of material strain mapping and diffraction on a Neolithic bronze axe as well as replicated material for noninvasive analysis. The main goal of the described investigations was to identify the effects upon the bronze objects of post-cast surface treatment with stone tools and of heat treatment.

1. Introduction

Neolithic and Bronze Age copper and bronze axes are part of our cultural heritage and due to their use as tools, weapons and status symbol good representatives of the state of the art of the ancient metal workers. During the Neolithic time period the previously exclusive stone tools were successively replaced by new materials [1], first copper, then bronze and new methods of production were developed and improved [2]. Being from a time without written documents in northern Europe, objects are the prime source of knowledge with respect to metal working. It is therefore best to carry out investigations in nondestructive ways, keeping the objects preserved for future generations. For a long time, available methods for investigations of the fabric of the objects were limited to sampling and the inspection of polished section. Fortunately that changed and investigation of texture and strain in historic axes was performed using neutron time of flight and neutron diffraction mainly in the last decade [3–6]. Advantages of those methods are the obvious noninvasive approach and the high resolution of phase contrast of the diffraction measurements, as well as bulk sensitivity, which may limit the effects upon the measurement of potential surface corrosion layers. The achievable spatial resolution of neutron investigations is usually limited due to flux and extent of neutron beams (typically in the range of some mm or above). Additionally, bombarding objects with thermal neutrons may radioactively activate the object. We chose an approach which is slightly less accurate concerning the absolute strain measured in the sample, but as we will show in the paper, it helps to easily distinguish the three main states that copper and bronze axes may be in: cast, forged and tempered (after previous cold working). Forging or cold working of bronze leaves visual imprints at the object's surface, which remain unchanged for the eye after tempering. The main advantages using X-rays are the possibility of using any spot size for the measurement from cm^2 down to some 100 μm^2 allowing integrative as well as local measurements, without any chance of activating the specimen chosen or damaging it in any other way. It should be noted that sample penetration depth of X-rays depends on the photon energy applied and in the here presented method is surface sensitive with less than 100 μm penetration depth. For similar applications one should consider that corrosion as patina, surface treatment e.g. with a punch and grain size distribution due to different casting methods may have significant contribution to the measurement. The chosen historic object had the patina completely removed upon finding and the replicated objects were all manufactured identically and cleaned, to investigate the effects of post-cast treatment. The specimens investigated were six replicated objects from the experimental archeological group at Gottorf Palace in well-defined production states using replicated historic tools and an original axe, the Axe of Ahneby (2200–2000 B.C.). The measurements were performed at DESY (Deutsches Elektronen-Synchrotron, Hamburg, Germany) using Beamline G3 [7] at DORIS III.

In the following section the specimen and the experimental setup will be presented.

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* Corresponding author. Tel.:+49 4089985753.
E-mail address: Leif.Glaser@desy.de (L. Glaser).

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Fig. 1. The Anglo-Irish Axe from Ahneby, Kreis Schleswig–Flensburg, of the northern Late Neolithic (~2300–1700 B.C.). It is a bronze axe of 25 cm in length and a weight of 700 g. This outstanding object has become so popular that it was integrated in the coat of arms of the parish (top right).

2. Material and methods

The replicas to test the method were produced by the Archaeological State Museum Gottorf Palace (Schleswig, Germany) in cooperation with the Casting Museum Howaldtsche Metallgießerei (Kiel, Germany). Original bronze axes were from the archeological state museum. A special focus was on the effects of potential cold working at the Late Neolithic Axe of Ahneby.

The Axe from Ahneby (Fig. 1), Kreis Schleswig–Flensburg, belongs into the group of so called Anglo-Irish Axes of the northern Late Neolithic. In Schleswig–Holstein this is still a horizon where metal objects are very rare. With a length of 25 cm and a weight of 700 g bronze the axe is an outstanding object, and it had become so popular that it was integrated in the coat of arms of the parish (Fig. 1, top right). As an imported object it might have been made in a different production process as the local products.

The replicas had a bronze stoichiometry of the average of the Axe of Ahneby and were cast using modern techniques. The copper was melted at 1300 °C and then tin was added and mixed for 1–2 min, before the axes were cast in sand cast technique using a foundry ladle. No additives were used for the bronze, except a little carbon to bind the scoria for removal prior to adding tin. Objects were cleaned using brushes and water, while ridges were removed using flint tools. After the first measurements the specimen was cold worked using stone tools, replicated after Neolithic finds [8,9] and tempered in a muffle furnace at 700 °C. This temperature is comparable to a charcoal fire with moderate airflow. After each treatment cycle, strain measurements were carried out and two dimensional X-ray images highlighting grains (or coherent zones) in the sample were taken. The results were compared with measurements performed with the Axe of Ahneby.

For surface sensitive diffraction analysis, two related experiments were performed: one for strain analysis with the sin$^2\Psi$-method [10–13] using a scintillation detector and one method using the MAXIM camera [7,14] for spatially resolved analysis of the aligned (220) reflexes. The experiments were performed at the G3 beamline (Fig. 2a) with a monochromatic X-ray beam of energy $\approx$ 6.9 keV. Sin$^2\Psi$ measurements were carried out by θ–2θ scans at different χ angles in the so called chi-mode (χ equals Ψ here) on the (220) reflection with an incident beam extent of 3×3 mm^2. MAXIM images were taken with maximum incident beam extent of about 16×6 mm^2 at incidence angle ω of 15° to the sample surface, and thus illuminating a large sample area. Measurements with the MAXIM camera are carried out by illuminating the specimen with a broad (parallel) beam which typically illuminates an area of ~13 mm × 4–13 mm of the specimen (Fig. 3). A signal is measured by a CCD area detector with a multichannnel plate (MCP) in front. The MCP acts as a collimating device for each CCD pixel such, that for a given detector angle e.g. diffraction originating from multiple locations on the sample surface is measured in parallel. MAXIM assembles a silicon chip of total 1024×1024 pixel^2 with the pixel size of 13×13 μm^2 matching aperture of the MCP. Depending on illumination geometry, the resulting images correspond to an area of ~13×13 mm^2 on the sample surface at the best resolution possible. Note that e.g. in case MAXIM collects the signal at an angle off the sample surface normal, projection effects lead to a worse spatial resolution on the sample surface (direction parallel incident beam). In the presented measurements the actual resolution is 13×13.2 μm^2 with a specimen sample surface area of 1.7 cm^2 covered.

Analyzing two wide range 2θ scans taken first with the silicon point detector, effects on the different diffraction patterns due to cold working were investigated (Fig. 2b). We observed significant changes in both the (220) and (222) reflexes, while only small changes were found for all other reflexes within the given scan range. The (220) reflex was chosen because of its better angular position close to 90° in particular with respect to MAXIM camera setup constrains, to allow for comparisons/findings from both detectors and due to the increase of intensity upon cold working seen in the data. Diffraction images with the

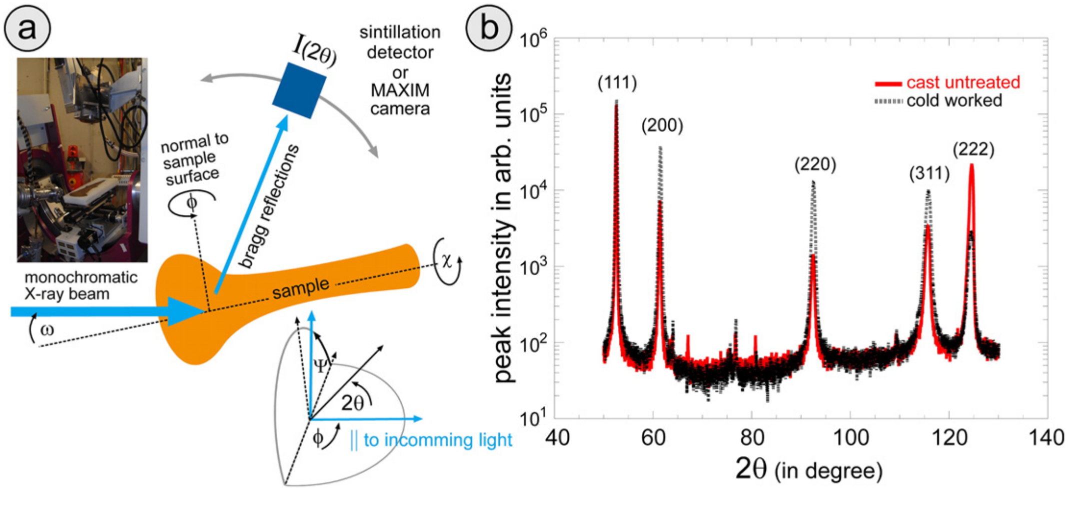

Fig. 2. (a) The experimental setup: The incoming monochromatic X-ray beam along the $2\theta = 0°$ direction hits the bronze axe in gracing incidence. The measurements can be performed using a MAXIM camera or a scintillation detector, which may move along a 2θ circle. When rolling the axe around the beam (χ equals Ψ) the surface stress tensor components $\sigma_{||}$ and $\sigma_{\perp}$ can be measured. (b) The effects of cold working of the bronze can be seen in the peak broadening of all reflexes, but also in the increase of the (220) reflex (at $2\theta = 92°$) and the decrease of the (222) reflex (at $2\theta = 124°$) of one order of magnitude each.