

Utilization of TEM in archaeology to gain in-depth information on historic artifacts

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Background incl. aims

Although inherently dealing with the past, archaeology has profited immensely from the use of modern advanced analysis techniques like electron microscopy [1,2]. Especially TEM can provide inaccessible insights, for example when only minuscule amounts of material are available or faint traces are studied [3,4]. Furthermore, the combination of in situ techniques (like heat treatment) with replicas can lead to vital insights into the exact methods and parameters used for the fabrication of historic artifacts.

In Sweden, two copper axes were found buried in the soil. Both axes were from the late neolithic and comparable to the axe found alongside "Ötzi". First measurements with X-ray fluorescence spectroscopy (XRF) indicated a silver-rich surface layer next to the obvious strong corrosion. These axes are historic artefacts and therefore a non-destructive sample preparation is necessary. A FIB cut TEM analysis of the surface layers could be carried out adhering to the strict rules of artifact preservation.

The very first settlers in Europe used cow dung as a reinforcement in pottery around 7000 B.C. Mechanical testing measured a higher mechanical strength at certain firing conditions for the reinforced pottery. Apart from the astonishing finding that composite (nano) materials were utilized at this time the exact nature of the strengthening mechanism is not known: is it mechanical (carbon fibres from the grass) or chemical (cow dung ash reacts with clay) in nature? Detailed analysis using TEM can help to better understand the mechanism as well as identify the fabrication procedure of ceramic artifacts.

Methods

The axes were first investigated via XRF and XRD to validate the field measurements. Additionally, the axes were loaded into a FIB-SEM and lamellae were taken out and analyzed via SEM-EDX. The FIB lamellae were subsequently analyzed utilizing a FEI Tecnai F30 G2 and a Jeol JEM-200F NEOARM.

In order to better understand the formation mechanism of silver enrichment and the corrosion layer a replica artifact was produced and artificially aged using suspension in humic acid for multiple weeks.

For the analysis of the reinforced pottery visible grass fibres were extracted with tweezers, ground in a mortar while suspended in butanol and deposited on the TEM substrate via drop coating. The same process was used for the archaeological sample, the unfired replica and several fired replicas. In addition a small amount of material was transferred onto an in situ heating chip (DENS solutions Wildfire) and heat treated up to 1100 °C in order to demonstrate the feasibility of in situ TEM observation of ceramic sintering and give insight into the mechanisms of the reinforced pottery during firing.

Results

XRD Rietveld analysis of the axe material showed a chemical composition in good agreement with XRF analysis. Since both techniques utilise X-rays the penetration depth is similar resulting in the same relative surface sensitivity. Analysis of the FIB-cut reveals the difference between the unoxidized bulk and the oxide layer, where in the CuO layer, precipitations of Ag are identified (see graphic). Additionally, the brittleness of the surface layer can be linked to the high amount of fractures visible in the CuO layer. The bulk material is uniform in contrast and has an Ag content of 0.8 at%.

In situ heating of a non-reinforced ceramic showed that for temperatures below 1000 °C the material showed a decrease in crystallinity as evidenced by loss of contrast in BF TEM and weaker diffraction rings in SAED. Above 1000 °C the material, which initially consisted of numerous crystallites, fused into larger crystals. Sophisticated background subtraction in rotational averages of the SAED patterns allowed their evaluation even for faint diffraction patterns.

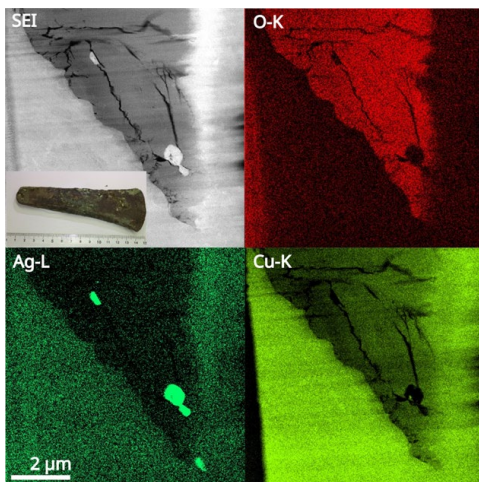
TEM analysis of the plant fiber reinforced ceramics did not reveal the presence of carbon nanofibers in the pristine as well as heated (in situ and ex situ) state. Carbon rich areas in the specimens could be found, yet not unambiguously linked to originate from the plant fibers. During heating no distinct differences to the non-reinforced ceramic were observed.

Conclusion

The investigation of the axes showed that the Ag-rich surface is a result of the corrosion process of the falutype copper, where the oxidization of the Cu reduces the AgO back to pure Ag, which then forms the grains visible in the EDS map. Consequently, the silver spots were not introduced deliberately, and thus, an initially ritualistic origin of the axes is disproven.

The feasibility of in situ TEM observation of ceramic sintering could be successfully shown. Due to the absence of carbon nanofibers for all sintering conditions mechanical reinforcement of the ceramic on the nanoscale can likely be ruled out. Due to the difficulty of unambiguously identifying specimen areas that originated from plant fibers the identification of the strengthening mechanism is the subject of ongoing investigation.

Graphic:



Keywords:

archeology, pottery, traceology, insitu, heating

Reference:

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