

# Storytelling: white layers on bronze

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## Introduction

In 2007, an extraordinary burial mount with the remains of the funeral of a very important man in prehistory has been excavated in the Netherlands. A large number of bronze decoration studs show uncommon white areas, next to more common green, black and red corrosion products (fig. 1).

### What stories do these white areas tell?

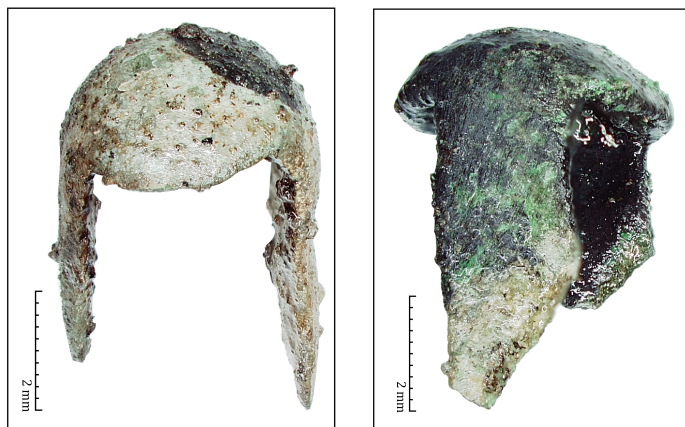


Fig. 1: Bronze studs with differently coloured areas (Early Iron Age,  $\pm$  600 BC).

## Experimental

Several analytical techniques were employed in this study<sup>†</sup> to deduce the biography of the bronze studs:

- Optical Microscopy (OM)
- Scanning Electron Microscopy (SEM)
  - + Energy Dispersive X-Ray Spectrometry (EDS)
- X-Ray Diffraction (XRD)

## Results & Discussion

The cross-section of an embedded stud leg (fig. 2A,B) displays the internal structure with detached grains. A continuous, optically white, outer layer is not adhered to the bulk. Zooming in on this layer yields a remarkable needle-like microstructure (fig. 2C,D).

Tin oxide ( $\text{SnO}_2$ ) is detected with XRD throughout the entire structure, no copper-tin phases are found. SEM-EDS measurements show the presence of tin (Sn), copper (Cu) and oxygen (O) in the top layer.

A tin-rich surface can have several origins:

1. During production, segregation of tin can occur during the cooling down after casting.
2. Deliberate tinning after forming the object will induce the presence of several copper-tin phases like  $\delta$  ( $\text{Cu}_{41}\text{Sn}_{11}$ ),  $\epsilon$  ( $\text{Cu}_3\text{Sn}$ ) and  $\eta$  ( $\text{Cu}_6\text{Sn}_5$ ).

3. Preferential corrosion of copper and/or the formation of tin oxide ( $\text{SnO}_2$ ) in the soil during burial.
4. A combination of an intentional high-tin surface (options 1-2) and oxidation (option 3).

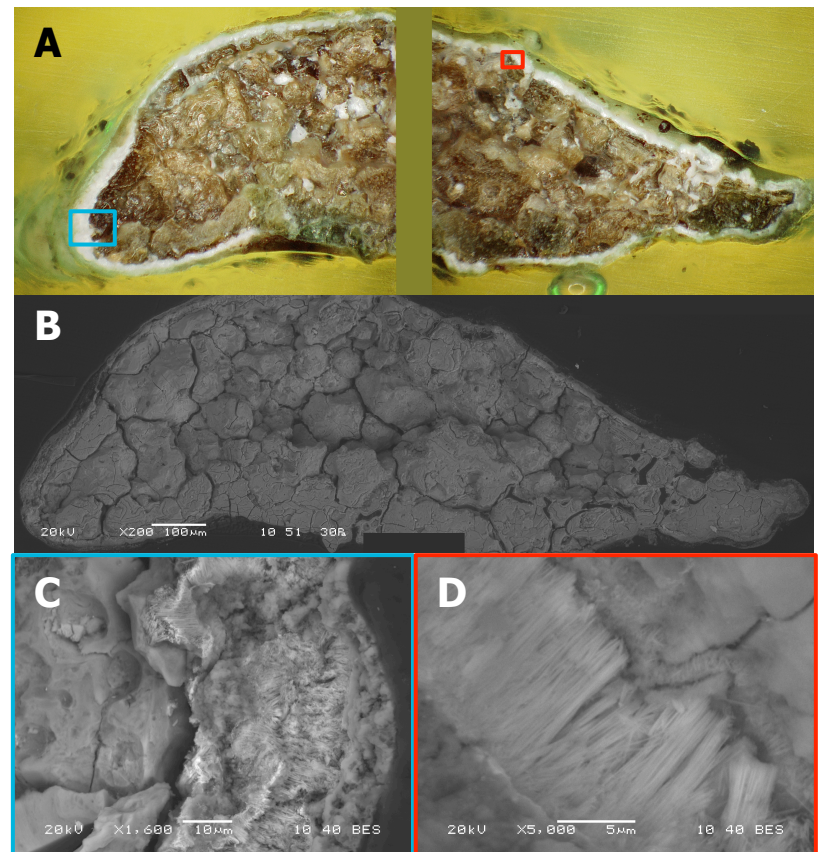


Fig. 2: Overview (A, B) and details (C,D) of the cross-section of an embedded stud leg, displaying the internal structures. A: Optical microscopy image. B-D: Backscatter electron images.

## Conclusion

The white areas are in fact tin-rich layers, also containing copper and oxygen. Its microstructure is needle-like and markedly different from the bulk. The corrosion product  $\text{SnO}_2$  seems to be present.

So the stories the white areas on these bronze decorations tell is that the studs were probably intentionally tinned, which has been worn off during use and oxidized after use.

## Further Research

The microstructure of the white, tin-rich layer needs to be characterised in more detail to distinguish between intentional tinning and corrosion.

<sup>†</sup> J. Nienhuis, J. Sietsma, D. Fontijn, I. Joosten, J. Dik, in press: Bronze studs: colouring, reconstruction, and conservation. In: D.R. Fontijn, S.A. van der Vaart, R. Jansen (eds.) **Transformation through Destruction. A monumental and extraordinary Early Iron Age Hallstatt C barrow from the prehistoric ritual landscape of Oss-Zevenbergen**, Leiden, Sidestone Press.