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METALLOGRAPHIC INVESTIGATION OF AN ANCIENT CHINESE HELMET

E.W. Schuring

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Made by: E.W. Schuring	Approved by: J.J. Saurwalt	Issued by: J.J. Saurwalt	ECN Technological Services & Consultancy

Acknowledgement/Preface

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Abstract

A cast bronze ancient Chinese helmet discovered in Chinese Mongolia in the Chifing district, was metallographically investigated to determine whether the pattern in the helmet was original to the helmet. Therefore, cross sections were made over the pattern. Under the pattern no plastic deformation that could be related to a mechanical method for engraving the pattern was found. The pattern is therefor believed to be original. Macroscopic examinations of the helmet and EDX-analyses on the cross sections were performed.

Keywords

Archaeology, Bronze, Casting, Chinese helmet, Metallography, Lost wax, Mongolia, Chifing, Zhou dynasty

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SUMMARY

An ancient Chinese helmet was submitted to ECN-TS&C-Materials technology for a metallographic examination. The bronze casting had a pattern on the surface. There were doubts about whether this pattern was original to the helmet. The metallographic investigation was focussed on the presence of plastic deformation under the pattern, which would point to a mechanical method for making the pattern in the helmet after it was cast. No heavy plastic deformation was found, indicating that the pattern is original to the helmet. The metallographic investigation further revealed the presence of oxides containing tellurium (Te), seleen (Se) and silver (Ag). The helmet's surface showed no evidence for the use of (complex) separable moulds, so it is concluded that most likely a clay model of wax model was used in a lost wax casting method.

1. INTRODUCTION

ArcheoPlan was asked to perform an investigation to determine whether an ancient Chinese army helmet was decorated with an original pattern. The helmet is believed to be made during the early (western) Zhou dynasty, 1100-600 BC. The finding site was located in Chinese Mongolia (Eastern Mongolia) in the Chifing district, North of Bejing. ECN-TS&C-Materials Technology was asked to perform the metallographic part of this investigation. Several small samples were cut from the helmet at ArcheoPlan and submitted for investigation.

2. EXPERIMENTAL

Before taking the samples, the helmet was investigated macroscopically to determine the locations best suitable for sampling. Four samples were taken from the helmet so that the samples included parts of the pattern in the helmet. Figure 2.1 shows an example of the sampling.

The samples were embedded and prepared for microscopic examination. The cross sections were examined for evidence of plastic deformation.

The reason for looking for plastic deformation or the absence of it, is that this can give indications about the manufacturing of the helmet. If the cross sections reveal severe plastic deformation, this would indicate that the pattern was mechanically engraved in the helmet after casting. Then there are two options, either the engravement was made immediately after casting and it is original, or it was made later, possibly many years, and is not original. Whether a mechanical engravement in the helmet was made immediately after production of the helmet or later can not be determined in this manner.
If the cross section is free of (severe) plastic deformation this indicates that the pattern was introduced during casting and it must be original.

Additionally, phases in the material were analysed by SEM/EDX.

The chemical overall compositions has already been determined and was supplied with the samples, see Table 2.1. The base material is a Copper-Tin alloy, Bronze.

Table 2.1 *Chemical analyses of the helmet base material*

Location	Remark	Fe	Co	Ni	Cu	Zn	As	Ag	Sn	Sb	Au	Hg	Pb	Bi
Helmet	Centre	0.26	<0.05	<0.06	89.2	<0.1	0.27	<0.05	7.1	<0.1	<0.03	<0.1	3.2	<0.05
Helmet	Surface	1.0	<0.05	<0.06	76.9	<0.2	0.57	<0.05	15.9	<0.1	<0.03	<0.1	5.6	<0.2
Animal	Surface	0.52	<0.05	<0.08	75.7	<0.1	1.3	<0.05	17.4	<0.1	<0.05	<0.1	5.1	<0.2


Figure 2.1 *Overview of the helmet and an example of the sampling*

3. RESULTS

3.1 Macroscopic examination

The helmet was macroscopically investigated for specific characteristics. The greater part of the helmet surface was covered with corrosion products. Some areas were free of corrosion products, as can be seen in Figure 3.1. Samples for metallographic examination were cut from such areas.

Figure 3.1 *Helmet outer surface for the greater part covered with corrosion products*

On the outer surface the ‘engraved’ pattern shows irregularities in the width of the engravement, see Figure 3.2. These irregularities show sharp changes in width. On the inner surface, locally the external pattern can be recognised as extrusions, see Figure 3.3. The surface of the helmet was free of markings that can be related to the use of separable moulds.

Figure 3.2 *Irregularities in the engravement. Locally the width of the pattern changes*

Figure 3.3 *Helmet inner surface, showing extrusions related to the pattern in the helmet. Also no evidence of rims related to the use of separable moulds*

3.2 Cross sections

The first two cross sections were characterised by severe corrosion. Almost the entire cross section was corroded so no definite conclusions could be drawn from this cross section regarding plastic deformation. Two other samples were taken from a less corroded area.

All cross sections show a microstructure typical for a casting, see Figure 3.4. The microstructure shows dendrites, indicating that the helmet was produced using a casting technique. Dendrites form during the solidification process of a casting. During cooling, solidification starts on nuclei, such as small impurities in the melt or at locations where because of the local chemical composition the melting point is higher. Starting from those nuclei the solidication process proceeds forming arms in arbitrary directions. This results in a structure resembling a little bit like ‘Christmas trees’ which after some time coincide when the solidified isles meet.

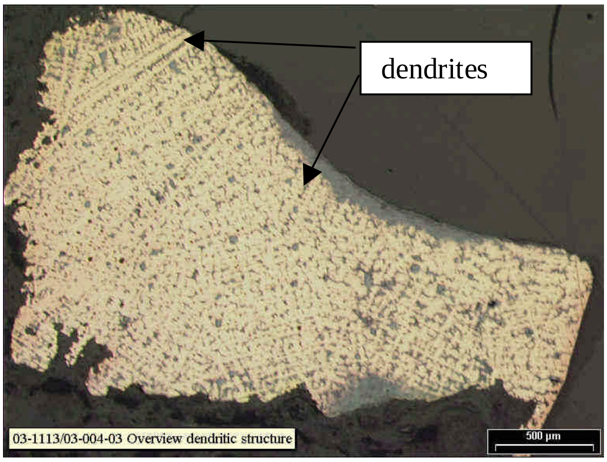

Figure 3.4 *Microstructure overview, indicating a cast microstructure with dendrites (03-1113)*

Several phases, most oxides, are present on the dendrite grain boundaries. Also some free Copper particles can be found in the microstructure, see Figure 3.5.

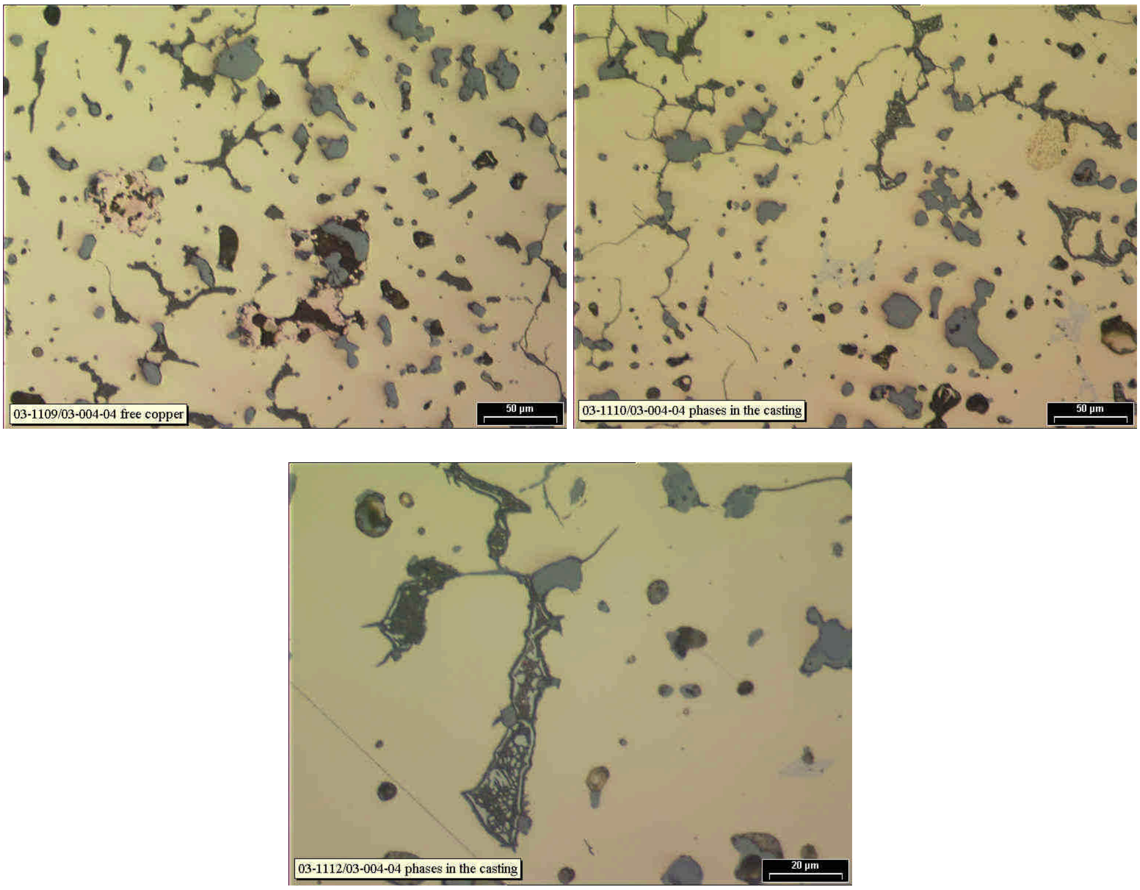

Figure 3.5 *Phases on the grain boundaries and free copper particles (03-1109/1110/1112)*

The cross section over the pattern shows a tappered shaped morphology, resembling the cross section of a riverbed, Figure 3.6. Under this pattern some minor plastic deformation of the dendritic microstructure can be recognised, however, this deformation is limited to a few microns and is of a local nature, Figure 3.7.

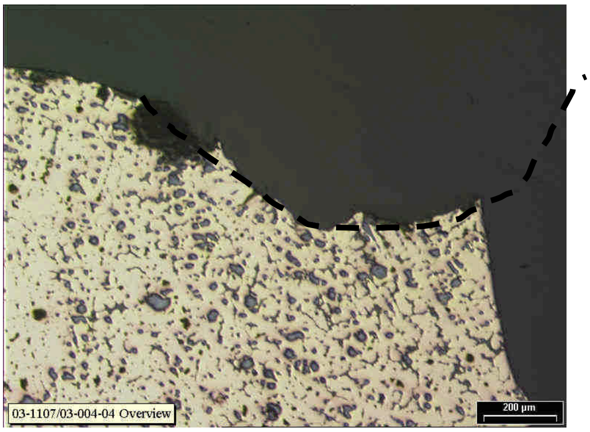

Figure 3.6 *Overview of the cross section over the pattern showing about the half of the riverbed shape (03-1107). The whole riverbed is schematically indicated by the dotted line*

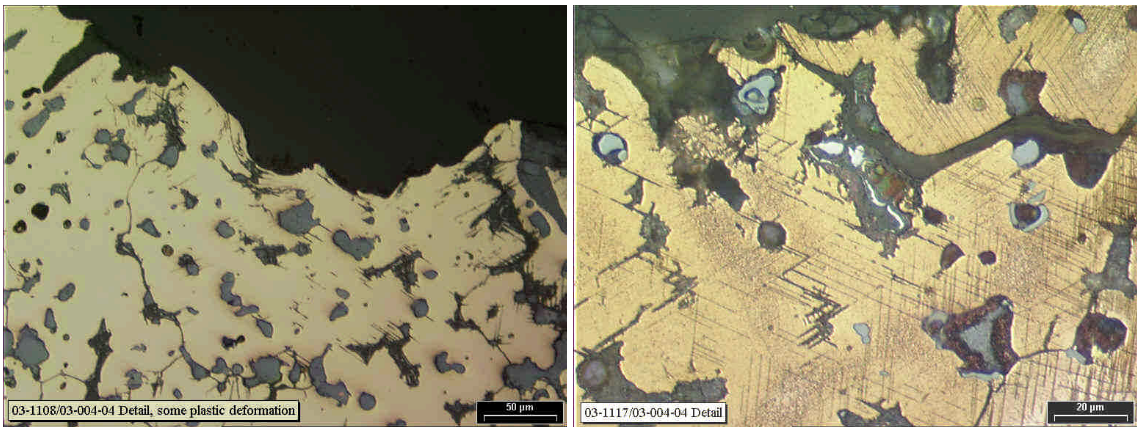

Figure 3.7 *Detail under the pattern, showing evidence of limited plastic deformation, unetched and etched (03-1108, -1117)*

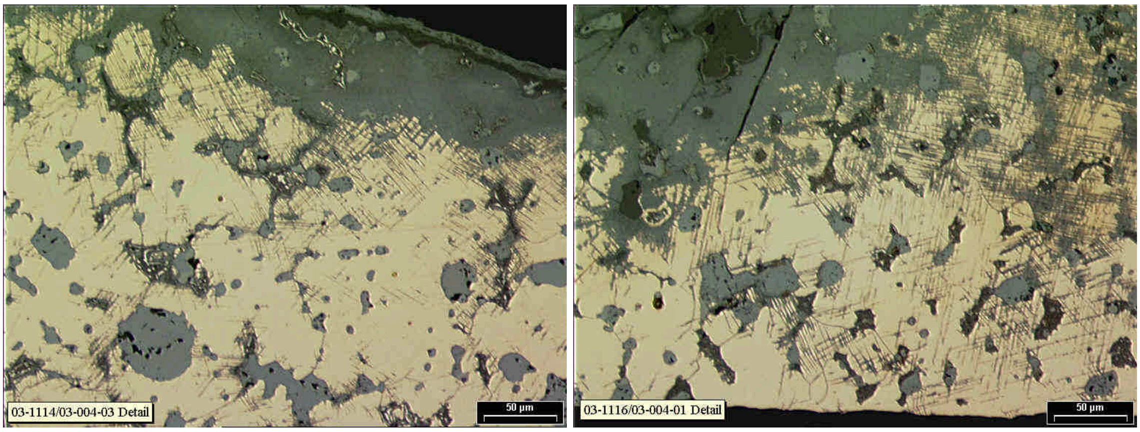

Figure 3.8 *Details of internal corrosion along crystallographic planes below the pattern (03-1114, -)*

Figures 3.7 en 3.8 show corrosion along crystallographic planes. This can be recognised by the following characteristics:

- The attacked planes run parallel to each other having a regular and distinct distance.
- The attacked planes show distinct angels to each other referring to distinct crystallographic planes.
- The attack is also found out side the patterned area.
- Below the pattern the attack is not more severe than outside this area, see Figure 3.8.

Another way to determine whether material was subjected to cold plastic deformation, as would be the case for mechanical engraving, is to determine the hardness of the material below the engravement and at a distance away from the engravement. Cold deformation of a metallic material will result in a significant raise in hardness. Hence, micro-hardness measurements were performed below the engravement, as shown in Figure 3.6, and at a distance as far away as possible in the same cross section. Hardenss testing was performed using the Vickers method with a load of 50 g, HV0.05. 5 Measurement were made per location. The results are presented in Table 3.1. From the results it can be concluded that no hardness increase has occurred below the engravement. The large scatter in data is caused by the fact the micro-hardness testing was used which has in inherent high scatter and the segregation in the casting, resulting in hardness differences over the cross section.

Table 3.1 *Results of the micro-hardness testing*

	Hardness (HV0.05)						
Location	1	2	3	4	5	Avg	S
Below engravement	135	87	115	108	97	108	18
Away from engravement	104	80	108	103	96	98	11

3.3 SEM-EDX analyses of the phases

In the microstructure several phases and particles can be identified. Figure 3.9 shows the EDX-analyses results of the analyses of these phases and particles. The analysed particles can briefly be described as, see Figure 3.9:

I. Sn-Pb-Cu-oxide
II. Cu-Te-oxide with traces of Se, Ag and S
III. Sn-oxides, with traces of S and Fe
IV. Cu-oxides, mainly the large rounded phases
V. Pn-Sn-oxides, small spherical particles

Within this investigation the phases were not to be identified in more detail. However, Se, Te and Ag may well originate from the Cu-ore used for this casting.

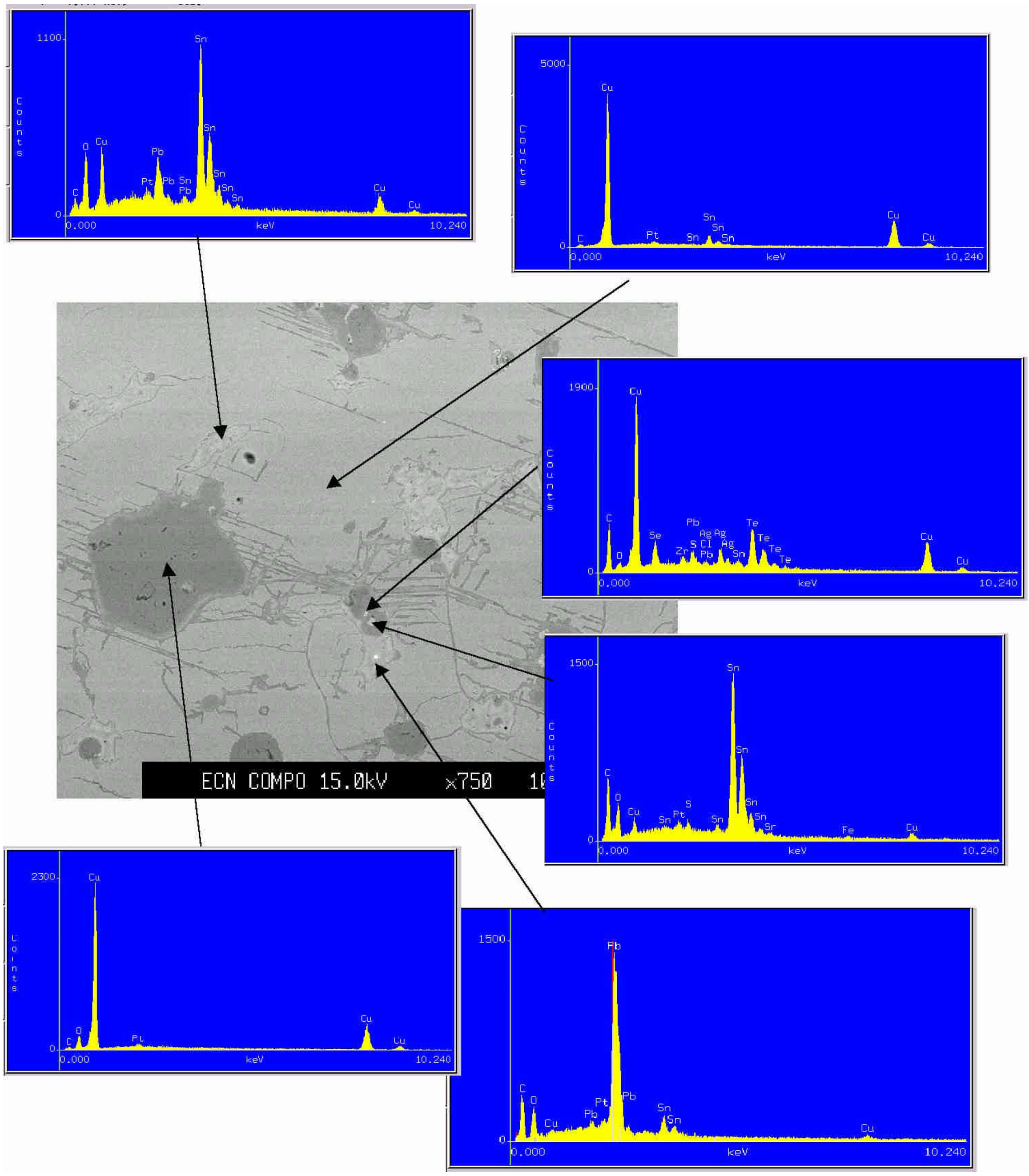

Figure 3.9 *Results of the EDX-analyses*

(NOTE: The Pt-indicated in the spectra originates from a Pt-Pd sputter coating applied to facilitate the EDX-analyses by enhancing conductivity of the embedded cross section)

4. DISCUSSION

To determine whether a pattern engraved in an ancient cast bronze Chinese helmet was original to the helmet, a metallographic examination was performed on cross sections over the engraved pattern in the cast helmet. The investigation was focussed on the presence of plastic deformation under or near the pattern. If the pattern were made by a mechanical method, this would result in severe plastic deformation in the cast microstructure. Considering the presence of extrusions in the helmet inner surface, apart from sliplines, also deformation of the dendrite structure should have occurred. Cross sections over the engraved pattern however do not indicate heavy plastic deformation of the microstructure. Micro-hardness measurements confirm that no cold deformation has occurred below the engravement and hence the engravement was made without mechanical machining of the helmet. The dendrite structure is relatively intact, accept for corrosive attack. This corrosive attack initiates along crystallographic planes in the bronze. So, therefor it is concluded that the pattern in the helmet was directly made by casting and is original to the helmet.

The helmet surface is free of rims that can be related to the use of a separable mould. Such a complex mould leaves rims on the surface on locations were the parts of the moulds come together. The absence of these rims indicates that the use of clay and sand possibly in combination with wax (the lost wax method) for the casting of the helmet. Other indications that may point to the loss wax method, are the irregularities in the in the helmet's pattern. Locally it appears like the maker of the helmet stopped to clean his equipment and than continued to remove wax of clay. At the locations where the maker stopped, a change in the width of the pattern occurs. From this assumption it was concluded a clay model and/or wax model was used in casting the helmet, in combination with wax, this is called the lost wax method.

In the microstructure, Se, Ag en Te were found concentrated in oxides, both intergranular and transgranular. These oxides were not investigated in more detail, but Te, Ag and Se are believed to originate from the Cu-ore. A more detailed investigation may give information on the mining site where the Cu-ore was taken from and the refining process used.

5. CONCLUSIONS

- The pattern in the helmet is original and fabricated during casting of the helmet.
- No plastic deformation below the engravement could be detected neither in the microstructure nor with hardness testing.
- Most likely a lost wax method was used for casting the helmet, since there is no evidence for the use of (complex) separable moulds.
- The presence of Te, Se and Ag in the bronze may give further information on the Cu-ore used and the refining process. This was not investigated in this report, but is recommended for future investigations.