# METALWORKING TECHNOLOGY AND DETERIORATION OF JIN BRONZES FROM THE TIANMA-QUCUN SITE, SHANXI, CHINA

CATALOGUE

# LIST OF CATALOGUE

## JIN BRONZES FROM THE ELITE TOMBS



## JIN BRONZES FROM OTHER CLASS TOMBS

## WESTERN ZHOU BRONZES FROM SHAANXI

# INTRODUCTION

The catalogue is produced as a separate volume for ease of presentation. It would be too repetitive to incorporate all data and photographs in the text, since some of the samples are mentioned more than one time. Furthermore, a large number of samples are discussed and grouped in several different ways.

The catalogue is divided into two groups: elite tombs and other class tombs. In each group, the subgroups are divided by the tombs, which are in sequence of date, with the earliest one being the first.

Each catalogue entry is divided into four sections: the general description, technical study of metal, the corrosion, and summary. The checklist of topics for each sample is shown in Table C1.

Not all photographic images are included in the catalogue for each sample due to limited space. The selection of photomicrographs illustrates characteristic features for each sample. Similar photographs for different samples are only shown to document similarities, but mentioned for other samples in catalogue texts. For example, the general view of fragments is shown for selected samples based on their peculiar shape, colour or corrosion morphology.

In the general section, illustrations of some objects are included in the general description depending on their availability from the excavators. The size of these bronze fragments is usually irregular, so the values given refer to the maximum length and width. The corrosion index refers to the depth of corrosion, ranging 1-5, in which 1 means a very thin corrosion layer on the object, 5 indicates severe corrosion (Chapter 4, Table 4.1). The estimated corrosion index is based on the metallographic observations. The colours of corrosion on the surface are described in general terms, e.g. green, red, blue etc. observed under the binocular microscope rather than laboratory colour scale measured by colour meter, because corrosion products are mixed and often contaminated by soil and charcoal. The decoration patterns shown up after investigative cleaning or radiography provide better object

identifications and typology.

Table C1 Checklist of topics for each sample

| Section | | Contents |
|---|---|---|
| **GENERAL** | Information: | Object number, type, date, excavation date, origin, fragment weight and size. |
| | Description: | Fragment shape, corrosion index, colour and surface decoration |
| **METAL** | Metallographic observation: | Object thickness, microstructure, grain size, inclusions and manufacture techniques. |
| | Composition: | AAS, microanalysis, and best estimate of bulk composition. |
| | Microhardness: | Vickers scale |
| **CORROSION** | XRD results: | In semi-quantitative order |
| | Metallographic observation: | Surface condition, interior corrosion, and corrosion layers on the surface |
| | Microanalysis: | Corroded metal, interior corrosion, and corrosion layers on the surface |
| **SUMMARY** | Alloy type, manufacture techniques, typology, corrosion status, features of interior and exterior corrosion. | |

In the section of technical studies of metal, the metallographic structure describes the thickness of the object, its microstructure, inclusions, grain size and manufacture techniques. The grain size is measured by intercept method using a metallographic picture or an electron image (see section 4.3.3). The composition includes either AAS and/or SEM/EDS data. AAS data were obtained for samples with sound metal, while SEM/EDS was done for corroded samples with small area of remnant metal. In some cases, both AAS and SEM/EDS data are included for choosing the best result. For heavily corroded samples, SEM/EDS data give a general idea about its original composition, for example, whether it was a leaded bronze. The micro-hardness is presented as Hv. Several photomicrographs of uncorroded samples are included to document their microstructure, inclusions, and evidence of working, etc.

In the section of corrosion, XRD results are listed in semi-quantitative order based on the intensity of the spectrum. The XRD result of corrosion products from the surface of M6190:3 is shown in Figure C1. The sequence of these corrosion products is: cerussite and $Pb_3(CO_3)_2(OH)_2$. It must be mentioned that this is only an estimation rather than accurate calculation. Quantitative analyses of corrosion products are judged beyond the scope of this project. Metallographic observations describe the extent of corrosion of the metal, the morphology and probable phase identification of corrosion products. Photomicrographs are included to show intergranular corrosion, pitting, corrosion layers on the surface, different types of corrosion in different parts of the same sample, and characteristic corrosion layer such as black layer, bronze disease, etc. Corrosion reflects archaeological context affected by burial environment, e.g. the construction and the depth of the burials, the location of an object in the burial and its surrounding environment. Microanalysis was mostly carried out using EPMA. The EPMA data, including metallic part are included in this part for full documentation and evaluation. EPMA and SEM/EDS data are as reported. These data are not normalised. Only 2 decimal places are significant for EPMA data. SEM/EDS data are reported as 1 decimal place (section 4.6.3). All compositions are expressed in weight percent unless otherwise noted.

The figures are numbered for each sample from figure 1 in the catalogue. When figures are referred to in the main text, they are referred to the catalogue number followed by the figure number. It needs to be mentioned here that if there is more than one piece for any objects, each piece is assigned the same number (object number) followed by a letter A, B, and so on. For example, M91:506A, Fig. 3 refers to Figure 3 of piece A of object M91:506, horse fitting/face ornament. In figure captions, BF denotes bright field; C/P, cross polarised light; BEI, backscattered electron image, and SEI, secondary electron image.

In summary, a very brief description of microstructure, composition, alloy type, manufacture techniques and typology is provided. The condition of the original surfaces, the features of interior corrosion and corrosion layers on the surfaces and are also stated.

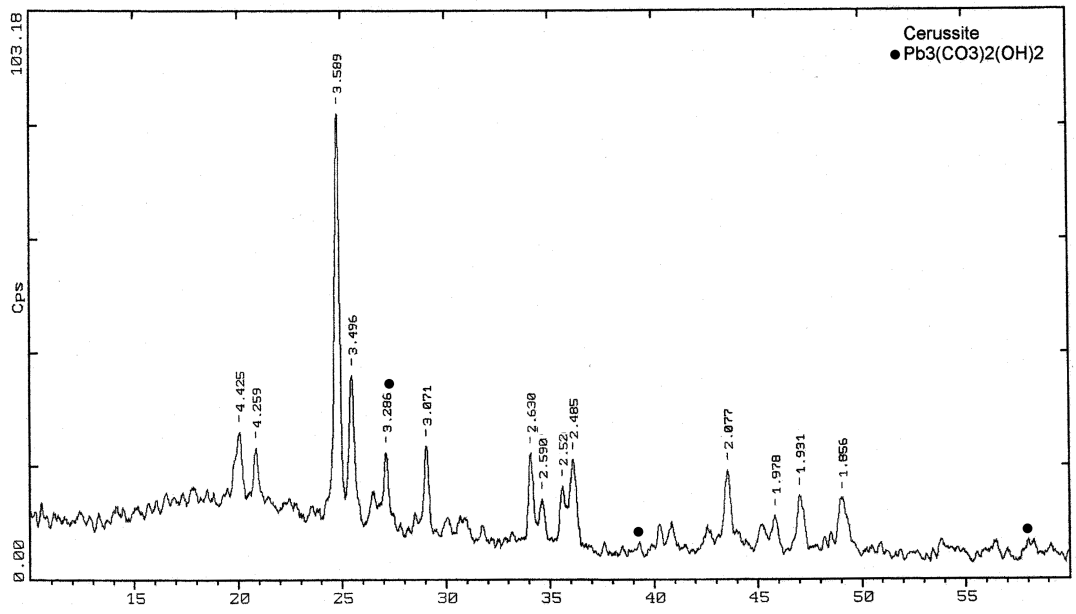



Figure C1 XRD spectrum of corrosion products on M6190:3

## GENERAL

**Object Number:** M9:313
**Excavation Date:** 1994
**Origin:** Tianma-Qucun site

**Object:** vessel/*ding*
**Date:** Middle Western Zhou
**Fragment Weight:** 1.3 g
**Fragment size:** 10x8x1.2 mm

**General description:**

This fragment has all sides broken. Corrosion index is 2. There is a corrosion overburden on the outer surface (convex), comprising mainly green (including fibrous type) corrosion products and soil. Bronze disease may also be present (at the left bottom corner) (Fig. 1). On the inner surface (concave), there is a very thin layer of corrosion. No decoration is apparent.

## TECHNICAL STUDIES OF METAL

**Metallographic structure:**

The original surfaces are disrupted, although most of the metal is intact (Fig. 2). The estimated thickness is 1.2 mm as measured in the metallographic section. It has an equi-axed structure with cuprite (proved by EPMA) on grain boundaries (Fig. 3). These cuprite dendrites were formed during casting rather than from corrosion process.

**Composition:**

**AAS:**

| Cu | Sn | Pb | Fe | As | Co | Zn | Ni | Ag | Au | Sb | Bi | total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ( | wt% | | ) | ( | | | ppm | | | | ) | (wt%) |
| 93.40 | 1.24 | 1.35 | 0.13 | nd | nd | 637 | 212 | 472 | nd | nd | nd | 96.25 |

**Microanalysis:**

See corrosion section.

**Microhardness:** 75Hv

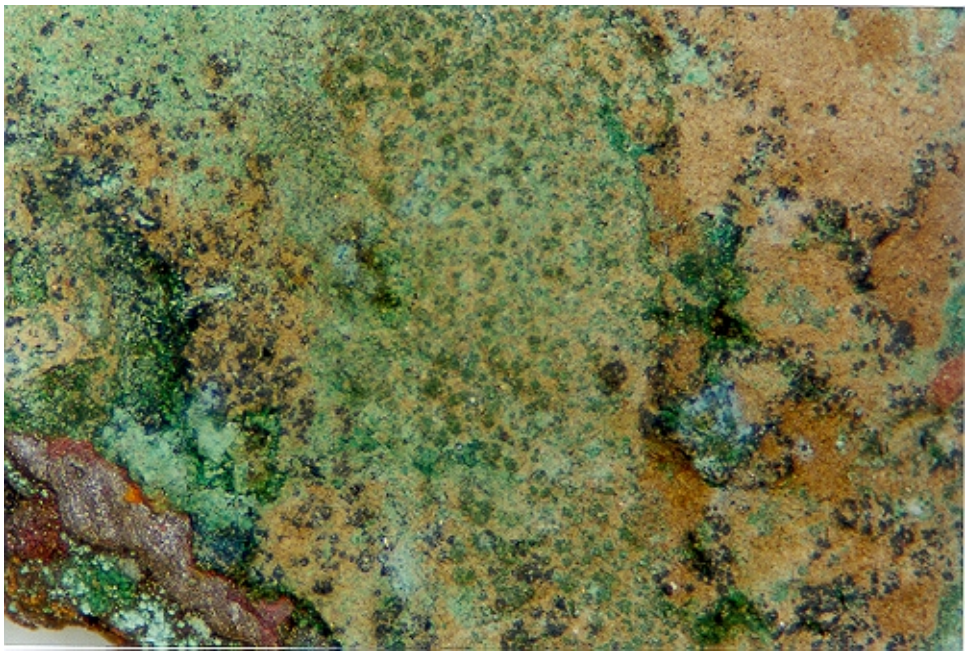


Fig. 1 General view of the fragment surface.
Width of the image = 4.2 mm.

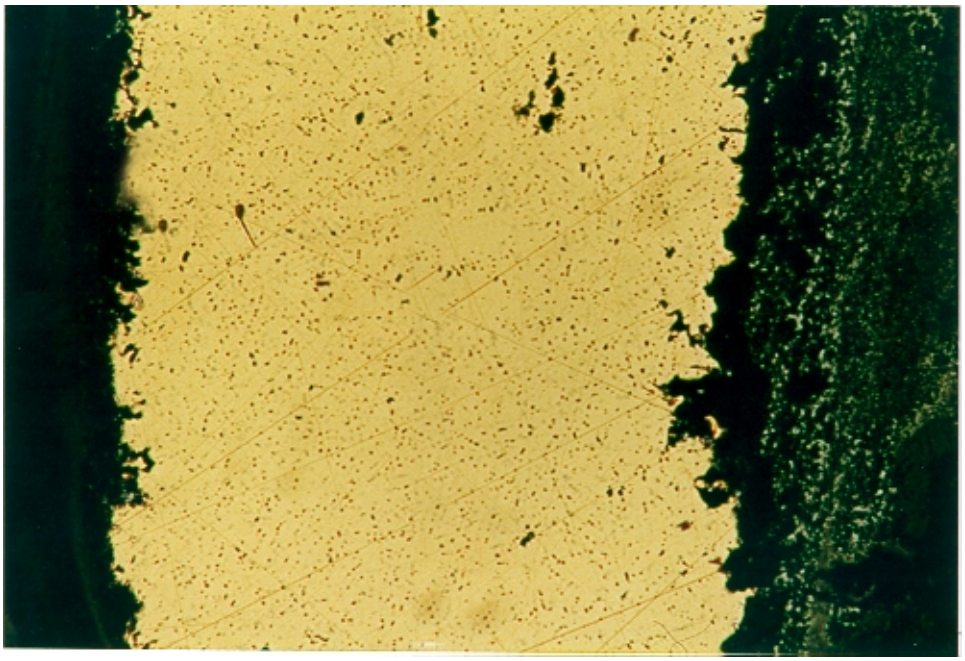


Fig. 2 Metallographic section, showing disrupted surfaces.
BF. Width of the image = 2 mm.

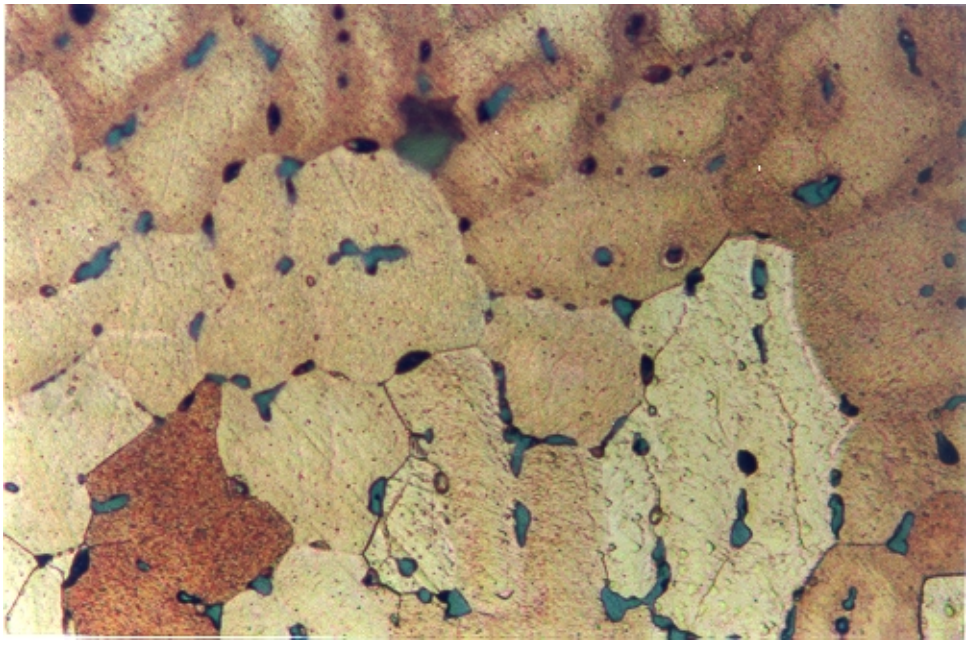


Fig. 3 Equi-axed microstructure, showing cuprite on grain boundaries.
Etched in aqueous $FeCl_3$. BF. Width of the image = 0.2 mm.

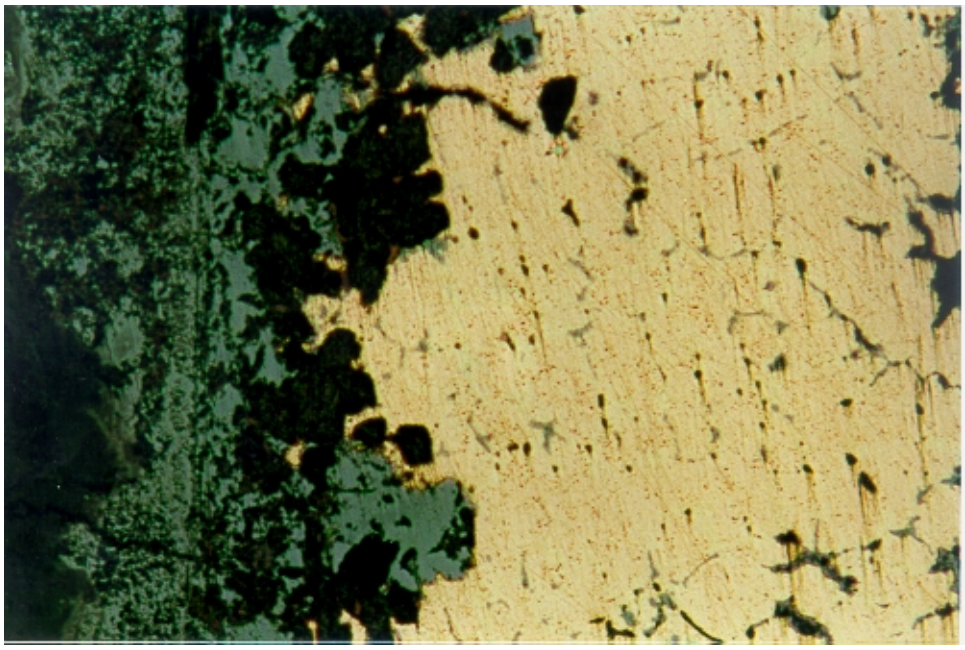


Fig. 4 Photomicrograph of disrupted surface by chloride.
BF. Width of the image = 0.5 mm.

## CORROSION

**XRD results:** not carried out

**Metallographic observation:**

On the outer surface where corrosion overburden is present, the original surface is disrupted by corrosion products although it can still be seen (Fig. 4). The grey one is cuprite based on its characteristic colour in the metallographic section. The darker one going further to the metal is likely nantokite.

**Microanalysis:**

Microprobe analyses were carried out on metal (Fig. 5) and the surface disrupted area (Fig. 6); the results are as follow. The darker corrosion mentioned above is relief in secondary electron image, and lower atomic number than its surroundings in backscattered electron image (Fig. 6).

| Point | Description |
|---|---|
| **1** | Lead inclusion |
| **2** | α phase |
| **3, 5** | Voids, partially filled with cuprite |
| **4** | Boundary between cuprite and α phase |
| **6, 7** | Nantokite |
| **8** | Cuprite |

| point | Cu | Fe | Au | Ni | Sn | Pb | Zn | Ag | Hg | As | Sb | Bi | Co | S | Cl | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 5.98 | 0.01 | 0.00 | 0.00 | 0.00 | 72.86 | 0.00 | 0.05 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 9.66 | 0.01 | 88.57 |
| **2** | 92.85 | 0.08 | 0.00 | 0.01 | 0.13 | 0.08 | 0.00 | 0.08 | 0.00 | 0.00 | 0.00 | 0.06 | 0.01 | 0.03 | 0.00 | 93.33 |
| **3** | 80.89 | 0.00 | 0.02 | 0.00 | 0.00 | 0.00 | 0.00 | 0.02 | 0.03 | 0.00 | 0.00 | 0.05 | 0.00 | 0.00 | 0.00 | 81.01 |
| **4** | 92.02 | 0.05 | 0.01 | 0.01 | 0.86 | 0.31 | 0.00 | 0.12 | 0.00 | 0.00 | 0.00 | 0.08 | 0.01 | 0.00 | 0.00 | 93.46 |
| **5** | 63.01 | 0.01 | 0.07 | 0.00 | 0.36 | 0.06 | 0.00 | 0.06 | 0.07 | 0.01 | 0.02 | 0.08 | 0.00 | 0.71 | 0.35 | 64.80 |
| **6** | 48.60 | 0.01 | 0.06 | 0.00 | 0.00 | 0.09 | 0.00 | 0.03 | 0.04 | 0.00 | 0.08 | 0.01 | 0.00 | 0.18 | 28.96 | 78.04 |
| **7** | 41.36 | 0.01 | 0.06 | 0.01 | 0.74 | 2.68 | 0.00 | 0.14 | 0.03 | 0.23 | 0.00 | 0.05 | 0.00 | 0.39 | 35.72 | 81.41 |
| **8** | 77.01 | 0.01 | 0.02 | 0.00 | 0.08 | 0.08 | 0.00 | 0.06 | 0.00 | 0.01 | 0.00 | 0.01 | 0.00 | 0.01 | 0.08 | 77.39 |

The ratio of Cl/Cu is close to nantokite, but much higher than that of atacamite. These data combined with its appearance suggests that the darker corrosion product in Fig. 4 and Fig. 6 is nantokite, which has not yet developed to bronze disease. Cl was not detected on the inner surface by EPMA.

The presence of lead is apparent in the backscattered electron image (Fig. 5). However, it is only 1.4 % in the bulk metal detected by AAS. It is likely the lead was from copper ore as an impurity. It solidified last to form on the grain boundaries.

**SUMMARY**

It is a copper object with Sn and Pb in low concentration. Pb is present on grain boundaries and as small droplets. Cuprite on the grain boundaries was from casting rather than from corrosion process[1]. This object with presence of $Cl^-$ would be expected to become active with inappropriate RH condition in storage or display.

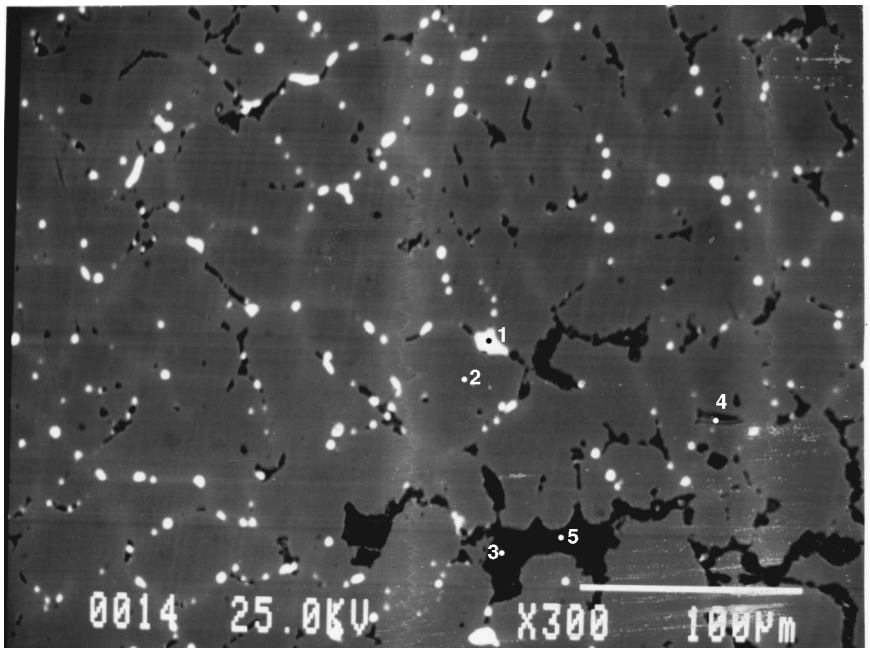



Fig. 5 BEI of metal, showing EPMA points.

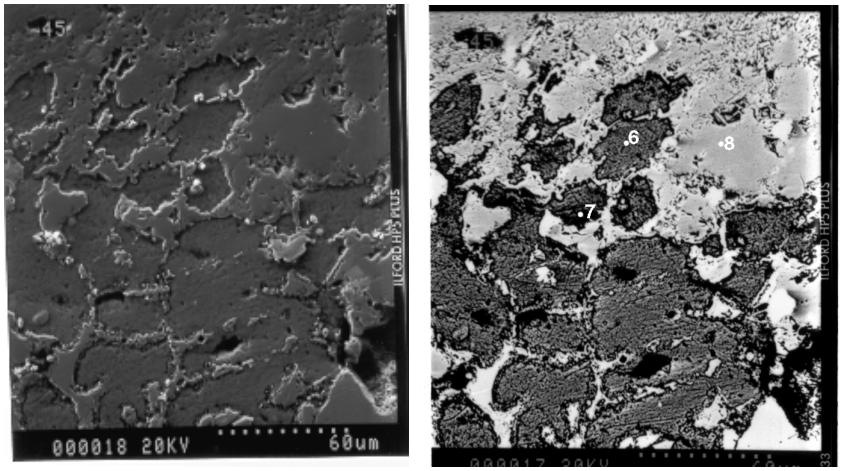



Fig. 6 Electron image of nantokite, confirmed by EPMA. Left: SEI; Right: BEI

[1] I thank Dr. J. Charles for this interpretation.

## GENERAL

**Object Number:** M9:401
**Excavation Date:** 1994
**Origin:** Tianma-Qucun site

**Object:** vessel/*zun*
**Date:** Middle Western Zhou
**Fragment Weight:** 1.5 g
**Fragment size:** 21x12x1.8 mm

**General description:**

This fragment has all sides broken. Corrosion index is 4. There is a thick corrosion overburden on the surface, including green, blue and black corrosion products. Soil is also present. Fibrous malachite is observed as well. No decoration is apparent.

## TECHNICAL STUDIES OF METAL

**Metallographic structure:**

The flat surface of the metallographic section (Fig. 1) suggests that this fragment was from a flat part of the object such as the base. Most areas of the metal except the far right part in Fig. 1 is corroded. The estimated thickness of the fragment is 1.8 mm as measured in the metallographic section. The original surfaces can be seen on both sides, although corrosion went all the way through the section. It has a cast dendritic structure (Fig. 2). The presence of very long dendrites indicates it was cooled slowly.

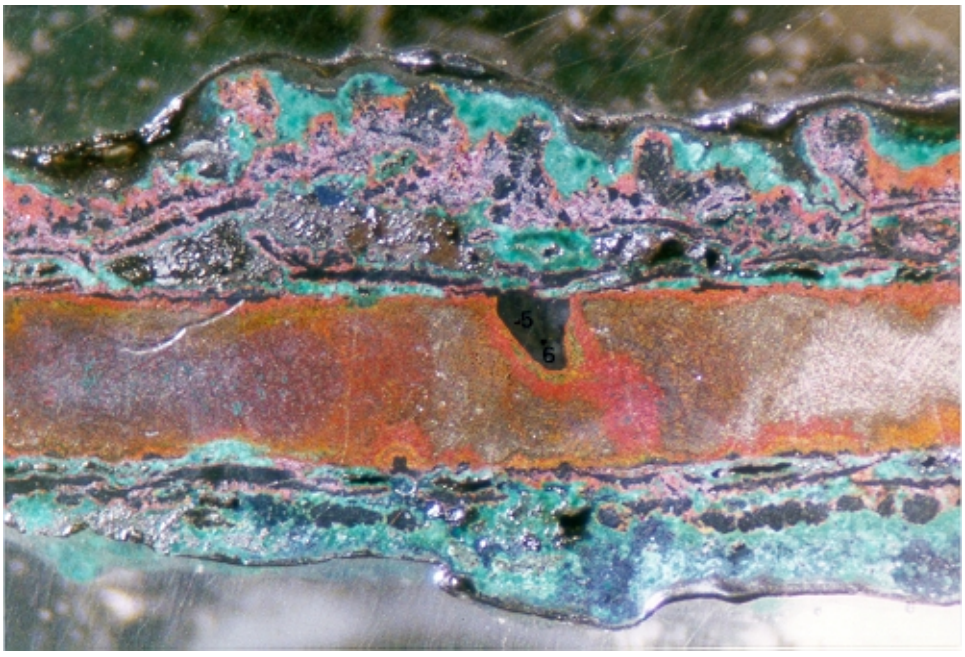



Fig. 1 The metallographic section, showing thick corrosion overburden and EPMA points 5 & 6. Width of the image = 10 mm.

Fig. 2 Dendritic microstructure. BF. Width of the image = 2mm.

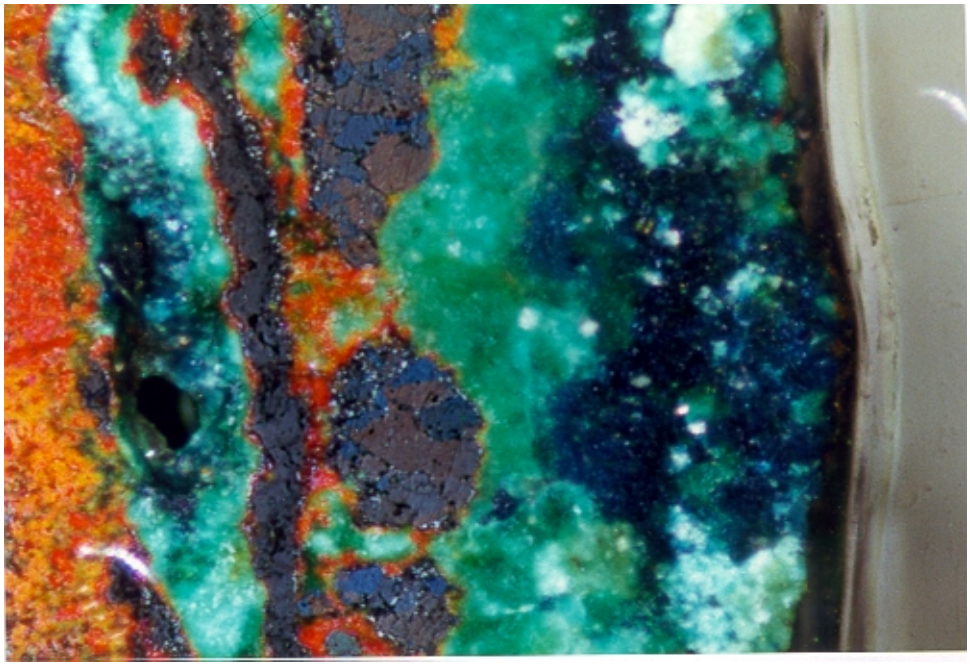


Fig. 3 Photomicrograph of corrosion overburden.
C/P. Width of the image = 2 mm.

## Composition:

**AAS:** too corroded for analysis

**Microanalysis:**

SEM/EDS semi-quantitative analysis was carried out on both uncorroded metal and corroded metal; the results are as follows:

| Uncorroded metal: | | | | Corroded metal: | | | |
|---|---|---|---|---|---|---|---|
| **Cu** | **Sn** | **S** | **Total** | **Cu** | **Sn** | **S** | **Total** |
| 82.2 | 13.4 | 0.3 | 95.9 | 57.3 | 22.5 | 0.4 | 80.2 |

**Microhardness:** 116Hv

## CORROSION

**XRD results:** not carried out

### Metallographic observation:

Most of the metal is corroded, with α remaining but δ being corroded off (Fig. 2). Corrosion overburden on both surfaces is thick (about 2 mm) (Fig. 1). Based on their characteristic colours in the metallographic section (Fig. 3), the corrosion overburden is comprised of cuprite, malachite, azurite and sulphide.

### Microanalysis:

EPMA was carried out on uncorroded metal, α core is clearly seen in backscattered image (Fig. 4), and sulphide inclusions are also present. EPMA was also carried out on 2 points of the black triangular area (Fig. 1); the results are as follow:

| Point | Description |
|---|---|
| **1** | α core |
| **2** | Edge of α phase |
| **3** | Eutectoid |
| **4** | Sulphide inclusion |
| **5, 6** | Sulphur-rich corrosion |

| Point | Cu | Fe | Au | Ni | Sn | Pb | Zn | Ag | Hg | As | Sb | Bi | Co | S | Cl | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 83.83 | 0.02 | 0.03 | 0.05 | 9.41 | 0.00 | 0.00 | 0.06 | 0.07 | 0.00 | 0.00 | 0.00 | 0.03 | 0.01 | 0.00 | 93.50 |
| **2** | 80.32 | 0.00 | 0.03 | 0.04 | 12.25 | 0.04 | 0.00 | 0.19 | 0.03 | 0.00 | 0.00 | 0.08 | 0.01 | 0.00 | 0.00 | 93.00 |
| **3** | 68.51 | 0.00 | 0.09 | 0.04 | 25.12 | 0.01 | 0.00 | 0.11 | 0.06 | 0.00 | 0.00 | 0.11 | 0.00 | 0.00 | 0.00 | 94.05 |
| **4** | 74.25 | 0.00 | 0.11 | 0.02 | 8.19 | 0.05 | 0.00 | 0.11 | 0.00 | 0.00 | 0.00 | 0.21 | 0.02 | 6.58 | 0.00 | 89.54 |
| **5** | 52.21 | 0.94 | 0.02 | 0.00 | 13.16 | 0.21 | 0.00 | 0.00 | 0.07 | 0.00 | 0.00 | 0.19 | 0.03 | 5.34 | 0.00 | 72.16 |
| **6** | 30.92 | 0.65 | 0.03 | 0.00 | 37.32 | 0.16 | 0.00 | 0.00 | 0.00 | 0.18 | 0.00 | 0.32 | 0.02 | 5.01 | 0.00 | 74.61 |

Like black layers appearing on surfaces of some other samples, this black triangular area is comprised of Cu, Sn and S, probably cassiterite mixed with copper sulphide, which formed in burial through time. Cl was not detected in this piece.

## SUMMARY

It is a binary alloy of Cu-Sn with sulphide inclusions. It has a cast dendritic structure. The best estimate of bulk composition conducted by SEM/EDS is 82% Cu and 13% Sn. Corrosion products are mainly copper carbonates, sulphides, cuprite and cassiterite.

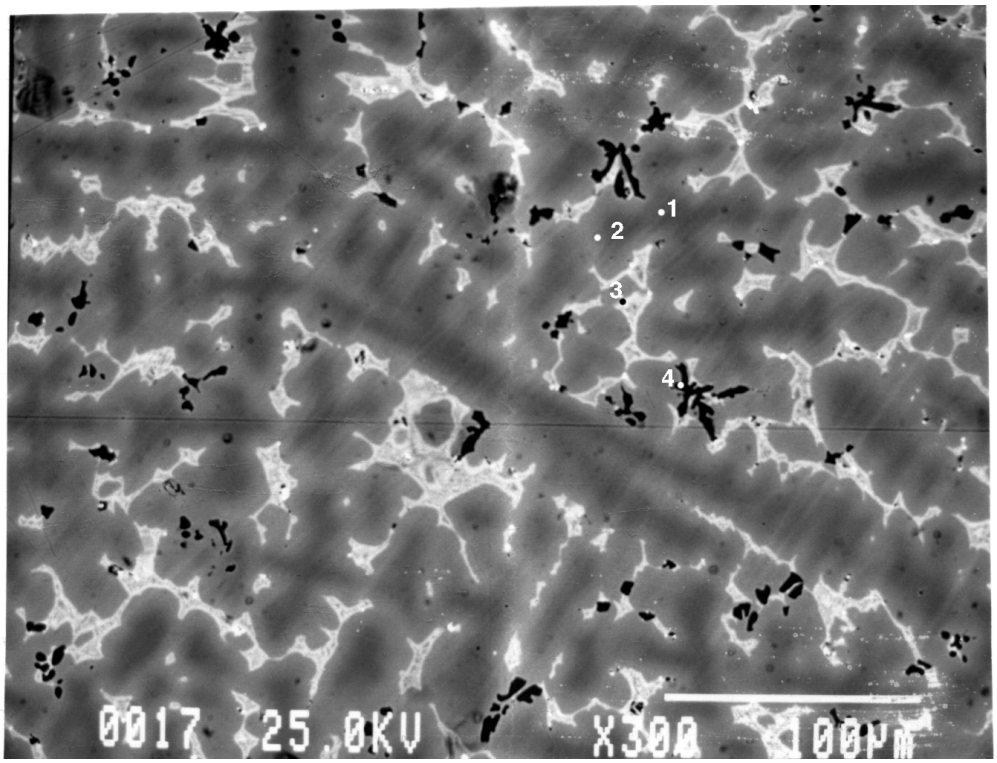



Fig. 4 BEI of metal, showing EPMA points.

## GENERAL

**Object Number:** M13:102
**Excavation Date:** 1994
**Origin:** Tianma-Qucun site

**Object:** vessel/*gui*
**Date:** Middle Western Zhou
**Fragment Weight:** 0.5 g
**Fragment size:** 8x5x1.6 mm

**General description:**

This fragment has all sides broken. Corrosion index is 2. There is a corrosion overburden on the surface. One surface is covered with green corrosion products and soil; the other one is covered with green, blue corrosion products and soil. No decoration is apparent.

## TECHNICAL STUDIES OF METAL

**Metallographic structure:**

The whole piece was mounted for metallographic observation. The original surfaces can be seen. The estimated thickness is 1.6 mm as measured in the metallographic section. It has a dendritic structure (Fig. 1), sulphide inclusions are present.

**Composition:**

**AAS:**

| Cu | Sn | Pb | Fe | As | Co | Zn | Ni | Ag | Au | Sb | Bi | total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ( | wt% | | ) | ( | | | ppm | | | | ) | (wt%) |
| 83.64 | 13.55 | 0.73 | 0.15 | 909 | nd | 515 | 515 | 909 | nd | nd | nd | 98.35 |

**Microanalysis:** not carried out

**Microhardness:** 116Hv

## CORROSION

**XRD results:** not carried out

**Metallographic observation:**

Corrosion went through the metal, δ phases are partially corroded. Redeposited Cu is present both inside the metal and in the corrosion on the surface (Fig. 2). Based on

their characteristic colours in the metallographic section, corrosion products are identified as cuprite, copper sulphide mixed with cuprite, malachite, azurite from the original surface outwards.

**Microanalysis:** not carried out

**SUMMARY**

It is a binary alloy of Cu-Sn, with a dendritic structure. Sulphide inclusions are present in the metal. The best estimate of bulk composition conducted by AAS is 83.6% Cu and 13.6% Sn. Redeposited Cu is present both inside the metal and in the corrosion on the surface.

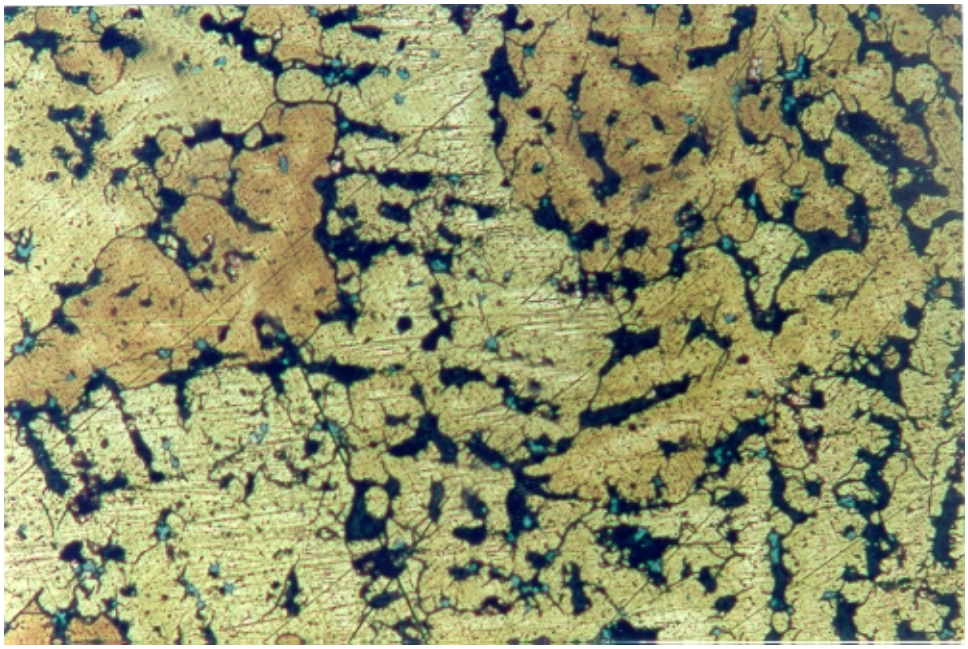


Fig. 1 Dendritic microstructure. Etched in aqueous $FeCl_3$.

BF. Width of the image = 0.5 mm.

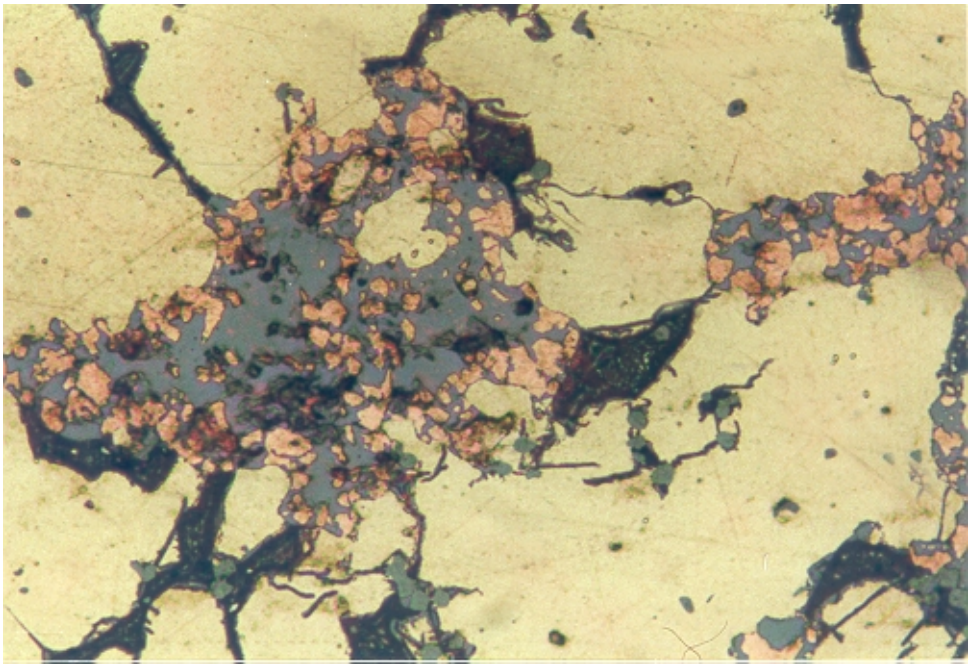


Fig. 2 Photomicrograph of redeposited Cu in cuprite.

BF. Width of the image = 0.2 mm.

## GENERAL

**Object Number:** M33:unknown 1
**Excavation Date:** 1994
**Origin:** Tianma-Qucun site

**Object:** horse fitting/*wei*
**Date:** Late Western Zhou
**Fragment Weight:** 15.8 g
**Fragment size:** 48x28x2.2 mm

**General description:**

This fragment has all sides broken. Corrosion index is 3. There is a corrosion overburden. The corrosion products on the surface are compact. They are pale blue, black and red. Black organic remains look like wood, probably charcoal. Red corrosion is seen at the edges where the outer layer of corrosion was peeled off. Fibrous corrosion products are also seen on the surface under binocular microscope. No decoration is apparent (Fig. 1).

## TECHNICAL STUDIES OF METAL

**Metallographic structure:**

A section cut through the full width of the fragment was taken for metallographic observation (Fig. 2). The estimated thickness of the metal is 2.2 mm. The estimated dendritic arm spacing is 0.067 mm. It is a cast dendritic structure (Fig. 3).

**Composition:**

**AAS:**

Sample for AAA was taken from the middle of the piece shown in Fig. 1 where the metal is less corroded.

| **Cu** | **Sn** | **Pb** | **Fe** | **As** | **Co** | **Zn** | **Ni** | **Ag** | **Au** | **Sb** | **Bi** | **total** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ( | wt% | | ) | ( | | | ppm | | | | ) | (wt%) |
| 75.20 | 11.15 | 1.92 | 0.453 | nd | 197 | 591 | 197 | 591 | nd | nd | nd | 88.88 |

**Microanalysis:**

See corrosion section.

**Microhardness:** 146Hv

Fig. 1 General view of the fragment. The metallographic sample was sectioned on the left side.

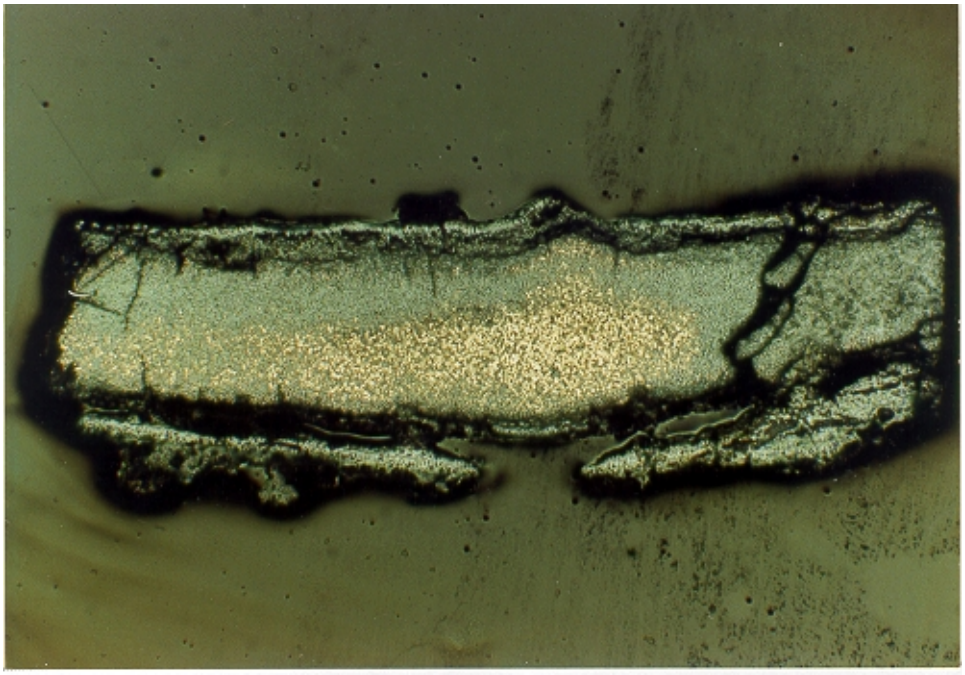


Fig. 2 The metallographic section. Width of the image = 10 mm.

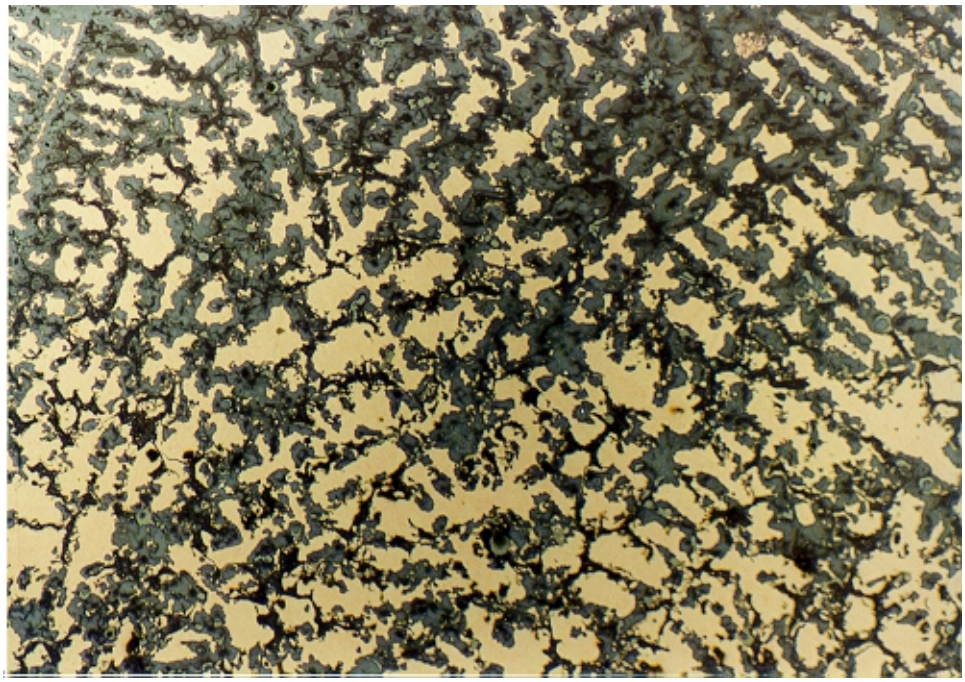


Fig. 3 Dendritic microstructure of corroded metal.
BF. Width of the image = 0.7 mm.

## CORROSION

**XRD results:** not carried out.

**Metallographic observation:**

Corrosion went all the way through the metal and resulted in δ-removal (Fig. 3). Corrosion overburden is up to 0.72 mm thick on one surface, but very thin on the other. Cracks broke the corroded metal all the way through from one surface to the other one in an area (Fig. 2). There is a black layer beneath copper carbonate, it looks like a part of corroded metal rather than corrosion overburden, for the interface between this layer and pseudormorphic dendritic structure is not apparent (Fig. 4). Copper sulphides are seen in the corrosion overburden (Fig. 5). Redeposited Cu is present in cuprite on the surface.

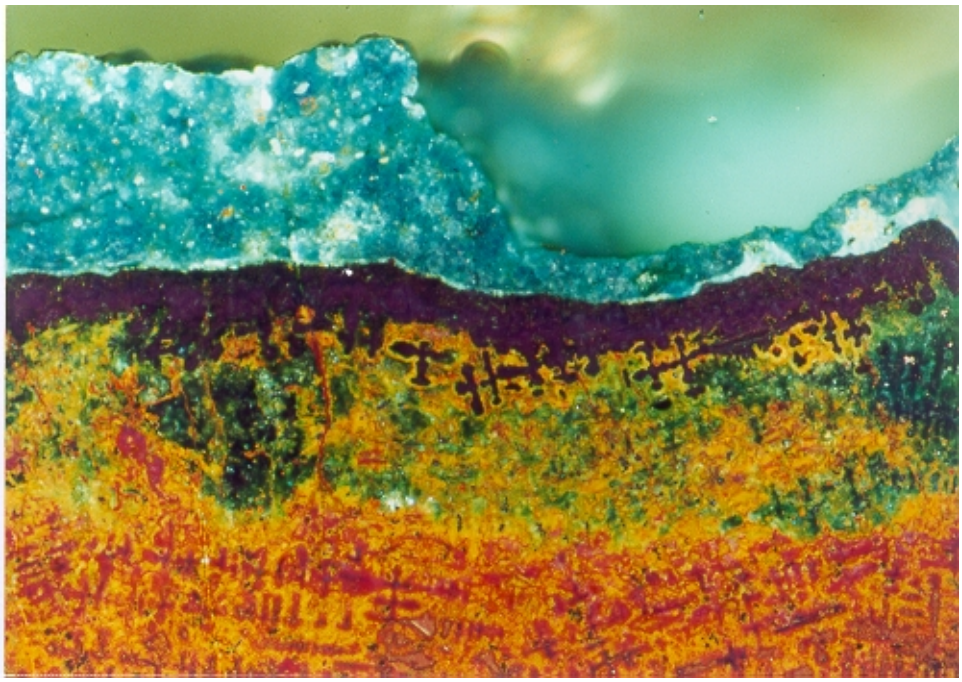


Fig. 4 Photomicrograph of black layer on the surface.
C/P. Width of the image = 1.4 mm.

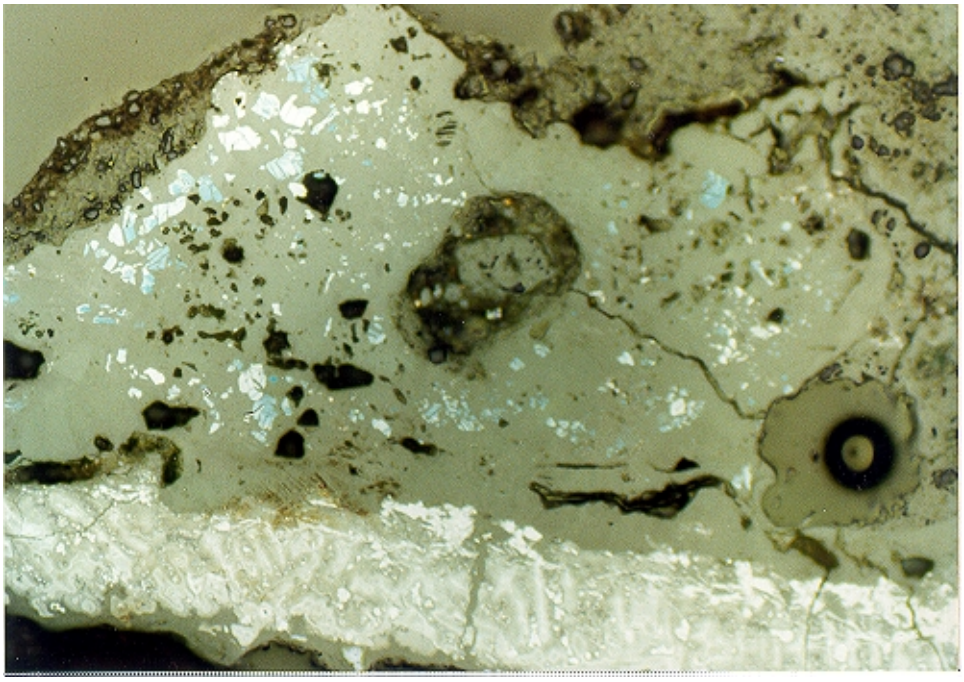


Fig. 5 Photomicrograph of sulphide crystals in corrosion overburden.
BF. Width of the image = 0.9 mm.

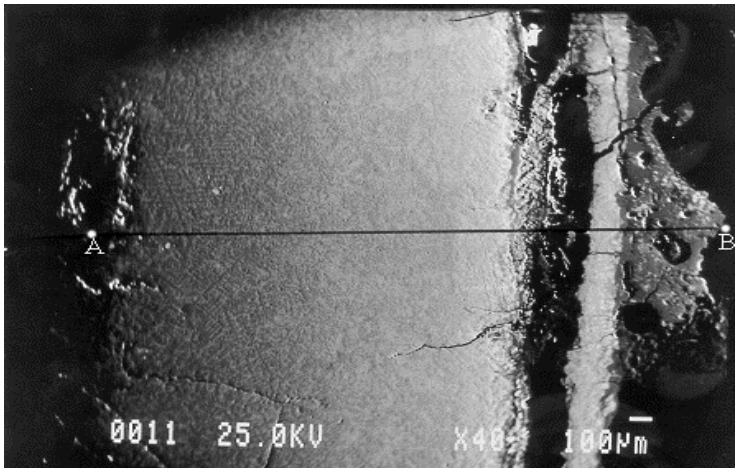
**Microanalysis:**

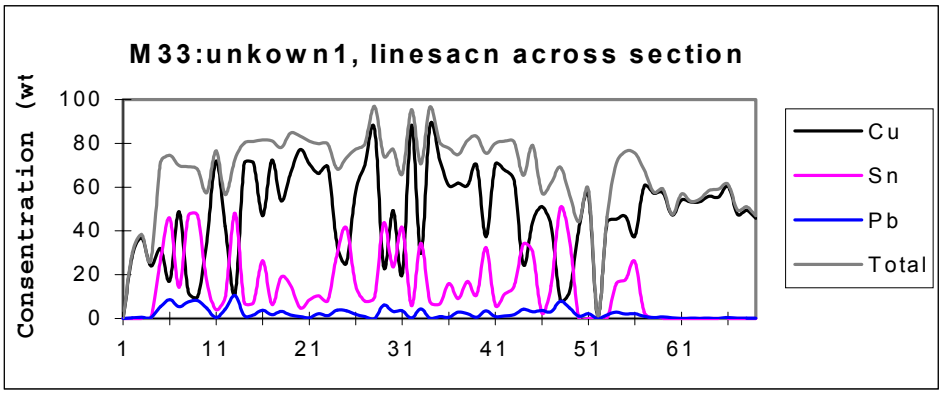
EPMA linescan across the entire metallographic section from A to B was carried out. The results are shown in Fig. 6. It contains Pb, with the maximum concentration being 10.5 %. Combined with AAS data, this object can be taken as a ternary alloy of Cu-Sn-Pb. Fig. 6 shows that Pb is present with Sn, this is due to its low melting point (232°C) and insolubility in Cu. Rich-Cu $\alpha$ phase with limited Sn in solid solution solidified first from liquid leaving excess Sn with Pb in the liquid to solidify later. Arsenic detected in corrosion layer is more than that in metal, while Cl is more in corroded metal than corrosion layer.

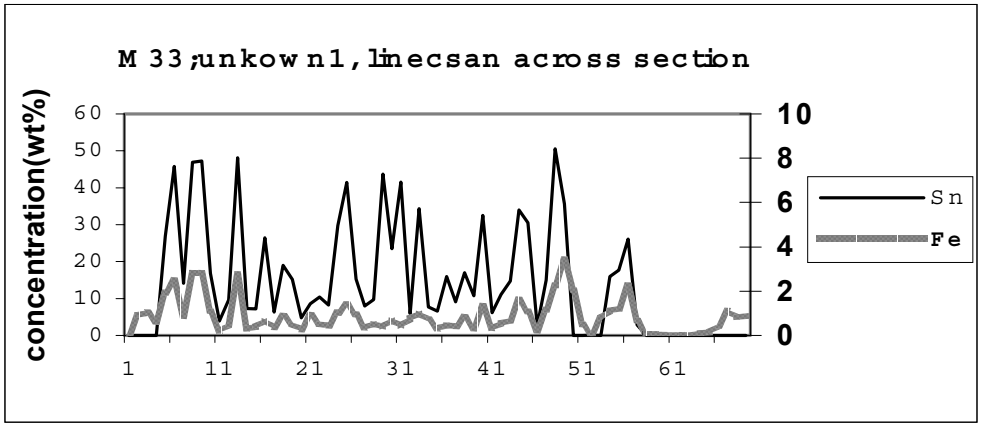
EPMA linescan across the black layer was also carried out. The results show that the black layer is rich in Sn and S compared with the metal (Fig. 7). Sulphur is associated with Cu, this suggests it is present as copper sulphide. Fe has the same correlation with Sn as that in metal. Discussion on this is carried out in chapter 6.

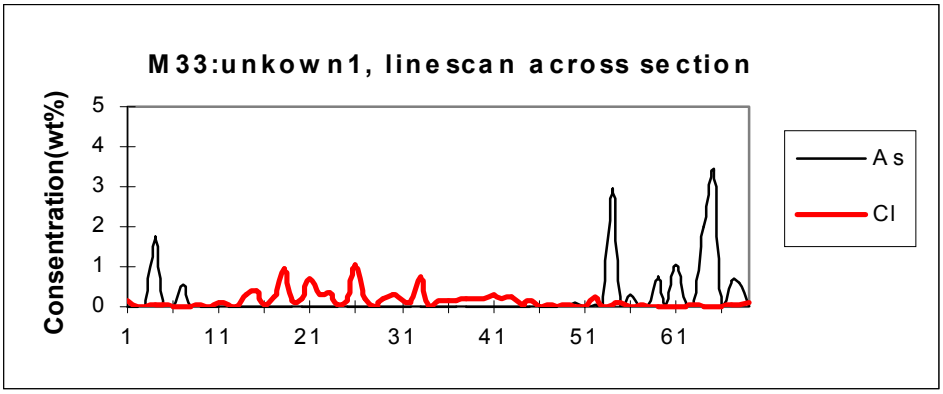
**SUMMARY**

The bulk composition conducted by AAS is 75.2% Cu, 11.2% Sn and 1.9% Pb. It is hard to say whether it is a binary or a ternary alloy due to its low AAS total, because the content of Pb is about 2%, which is considered as the border point between accidental and deliberate alloying used in some references (see Chapter 7). It is a cast dendritic structure. There is a black layer on the surface. Redeposited Cu is present in cuprite on the surface.


A
B
0011 25.0KV
X40
100µm


M33:unkown1, linesacn across section
Consentration (wt
100
80
60
40
20
0
1
11
21
31
41
51
61
Cu
Sn
Pb
Total


M 33;unkown1, linecsan across section
concentration(wt%)
60
50
40
30
20
10
0
10
8
6
4
2
0
1
11
21
31
41
51
61
Sn
Fe


M33:unkown1, linescan across section
Consentration(wt%)
5
4
3
2
1
0
1
11
21
31
41
51
61
As
Cl

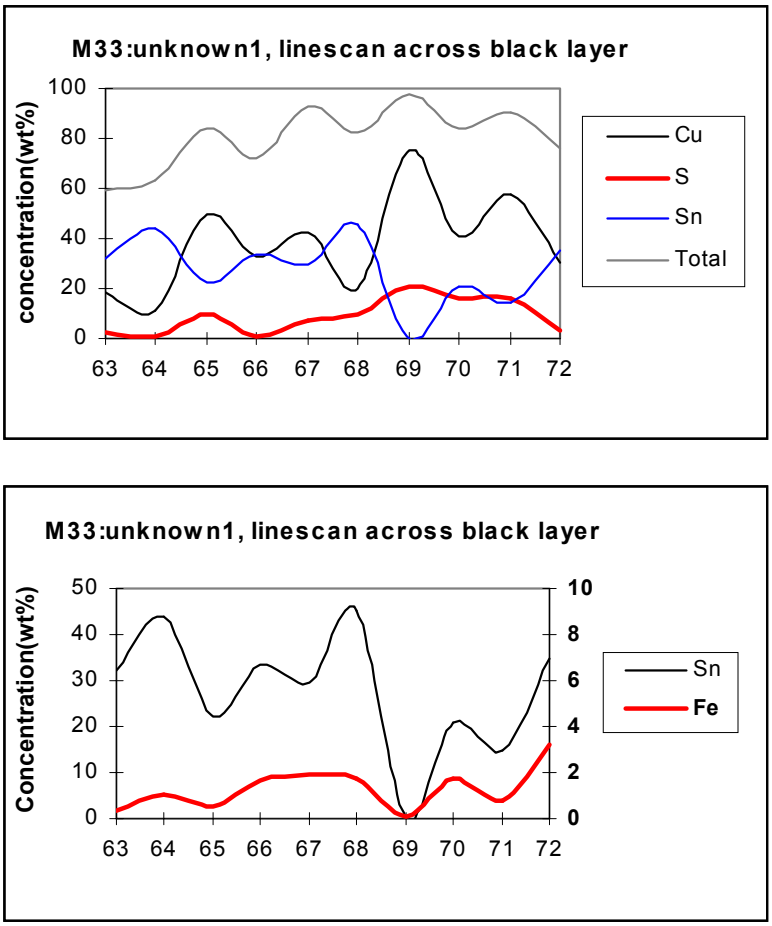



Fig. 7 EPMA linescan across black layer

## GENERAL

**Object Number:** M33:unknown2
**Excavation Date:** 1994
**Origin:** Tianma-Qucun site

**Object:** horse fitting/*luan* bell
**Date:** Late Western Zhou
**Fragment Weight:** 26.9 g
**Fragment size:** 42x28x(2.2–2.5) mm

**General description:**

This fragment has all edges broken except the shoulder. Corrosion index is 2. There is a corrosion overburden and soil on both the inner and outer surfaces, including green, blue, red and black corrosion products. There are cracks in the corrosion. No decoration is apparent (Fig. 1)

## TECHNICAL STUDIES OF METAL

**Metallographic structure:**

A section cut through the neck was taken for metallographic observation. The estimated original thickness is 2.2-2.8 mm as measured in the metallographic section. The original surfaces are preserved well, although corrosion has gone all the way through the section and resulted in visible cracks (Fig. 2). It is a dendritic structure (Fig. 3).

**Composition:**

**AAS:**

| Cu | Sn | Pb | Fe | As | Co | Zn | Ni | Ag | Au | Sb | Bi | total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ( | wt% | | ) | ( | | | ppm | | | | ) | (wt%) |
| 77.55 | 17.79 | 0.120 | 0.389 | nd | nd | 359 | 299 | 599 | nd | nd | nd | 95.97 |

**Microanalysis:**

See corrosion section

**Microhardness:** 190Hv

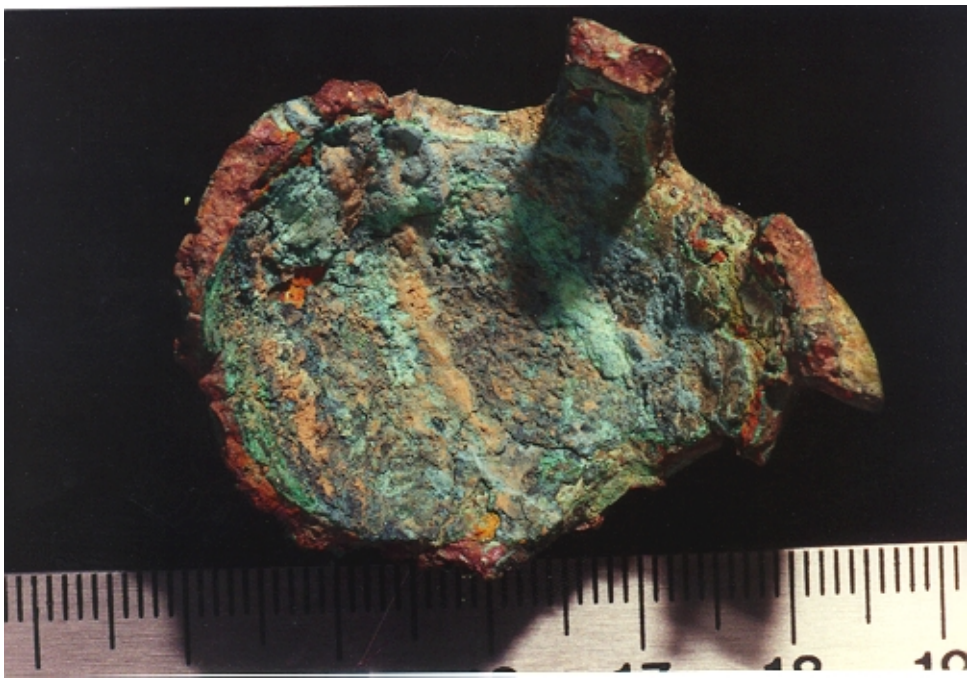


Fig. 1 General view of the fragment.

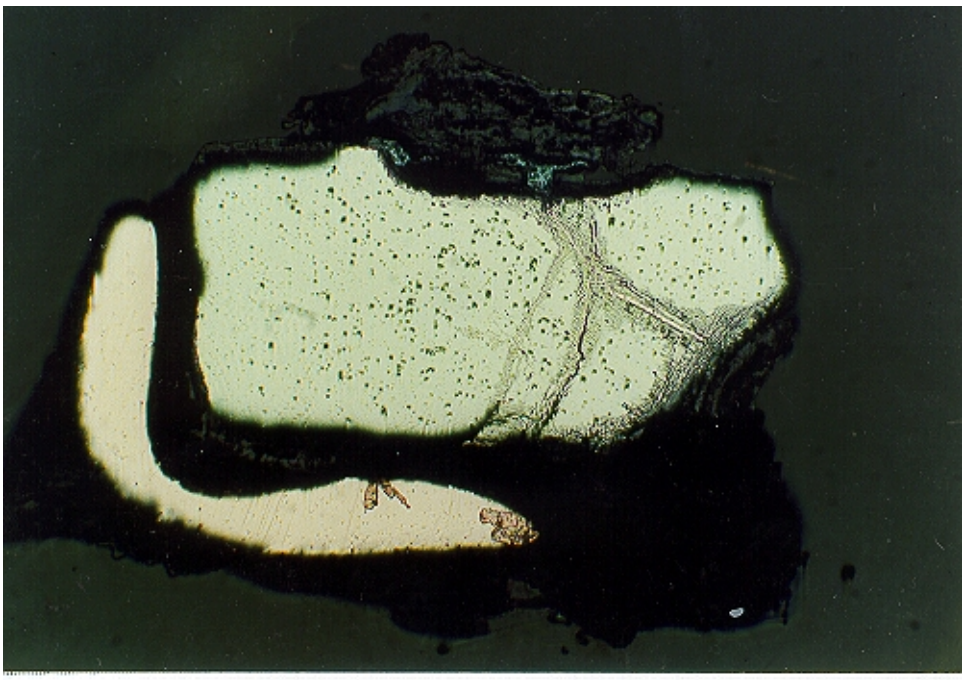


Fig. 2 The metallographic section. The biggest thickness of the sample = 2.8 mm.
The brass wire at left bottom corner is sample stand.

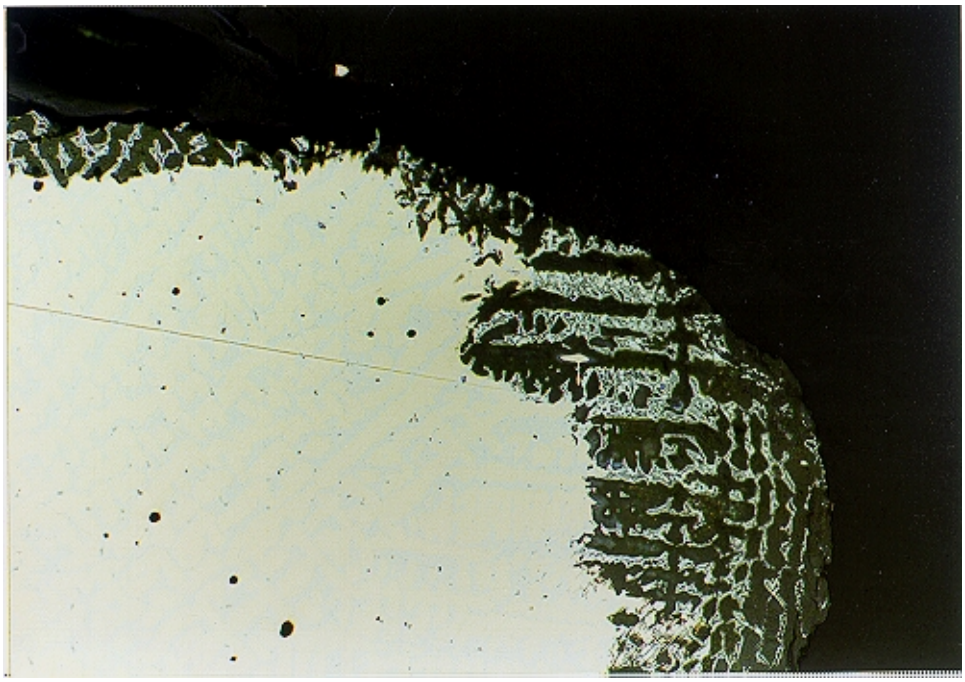


Fig. 3 Microstructure of corroded metal with α removal on the surface.

BF. Width of the image = 0.7 mm.

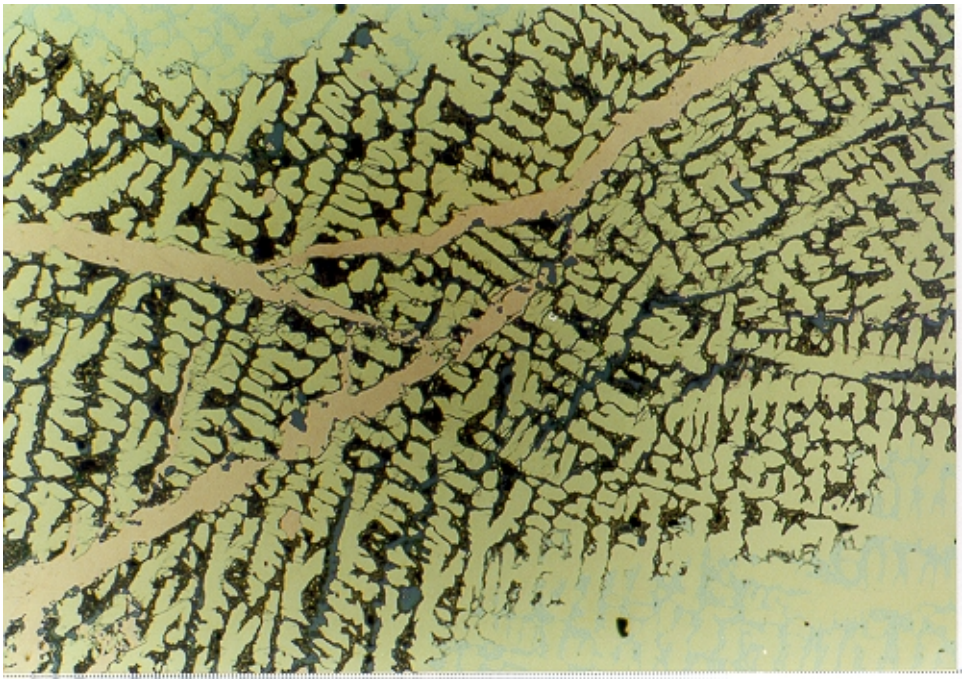


Fig. 4 Photomicrograph of redeposited Cu in δ removal area.

BF. Width of the image = 0.7 mm.

## CORROSION

### XRD results:

Surface sample: malachite, azurite, brochantite, cuprite, cassiterite.

### Metallographic observation:

Two types of corrosion, α-removal and δ-removal, are seen in this sample. α-removal corrosion is seen on the surface (Fig. 3), while δ-removal corrosion is seen inside the metal and around the cracks (Fig. 4). Redeposited Cu with twin lines is seen in the δ-removal corrosion areas (Fig. 5). Redeposited Cu can be visually seen in Fig. 2. Corrosion (mainly cuprite detected by EPMA) expanded and created fractures on the surface (Fig. 6).

### Microanalysis:

EPMA was carried out on the area of redeposited Cu in metal (Fig. 7) and on corrosion on the surface; the results are as follow:

| Point | Description |
|---|---|
| **1, 3** | Redeposited Cu |
| **2, 4** | α phase |
| **5** | Corroded eutectoid |
| **6, 12, 13** | Remnant δ phase |
| **7, 10, 11** | Corroded α phase |
| **8** | Corrosion, which broke the surface |
| **9** | The inner most corrosion |

| Point | Cu | Ni | Fe | Sn | Pb | As | Zn | Co | S | Cl | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 93.73 | 0.00 | 0.14 | 0.74 | 0.04 | 0.00 | 0.00 | 0.00 | 0.05 | 0.03 | 94.72 |
| **2** | 82.05 | 0.04 | 0.23 | 14.71 | 0.06 | 0.00 | 0.00 | 0.00 | 0.06 | 0.00 | 97.14 |
| **3** | 97.61 | 0.00 | 0.01 | 0.07 | 0.06 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 97.76 |
| **4** | 79.27 | 0.03 | 0.27 | 16.77 | 0.08 | 0.00 | 0.00 | 0.00 | 0.02 | 0.00 | 96.44 |
| **5** | 34.54 | 0.01 | 0.82 | 32.18 | 0.34 | 1.80 | 0.00 | 0.02 | 1.49 | 0.09 | 71.28 |
| **6** | 35.60 | 0.03 | 1.16 | 27.39 | 0.09 | 0.00 | 0.00 | 0.00 | 0.25 | 0.01 | 64.52 |
| **7** | 39.67 | 0.00 | 1.12 | 28.57 | 0.22 | 0.00 | 0.00 | 0.01 | 0.25 | 0.00 | 69.83 |
| **8** | 83.53 | 0.00 | 0.01 | 0.04 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.12 | 83.71 |
| **9** | 54.97 | 0.00 | 0.01 | 0.05 | 0.03 | 0.00 | 0.00 | 0.00 | 7.07 | 0.00 | 62.13 |
| **10** | 19.10 | 0.02 | 1.47 | 46.56 | 0.39 | 0.00 | 0.00 | 0.00 | 0.48 | 0.00 | 67.98 |
| **11** | 18.23 | 0.00 | 2.74 | 44.32 | 1.45 | 0.00 | 0.00 | 0.00 | 0.04 | 0.00 | 66.78 |
| **12** | 29.06 | 0.05 | 1.81 | 39.82 | 0.51 | 0.00 | 0.00 | 0.00 | 0.03 | 0.03 | 71.31 |
| **13** | 39.48 | 0.06 | 0.57 | 39.52 | 0.36 | 0.00 | 0.00 | 0.00 | 0.09 | 0.00 | 80.08 |

Comparing AAS data with EPMA data, it can be assumed that EPMA data of the uncorroded α phase approximately represent the composition of the alloy, with the Sn content being a little lower but Cu a little higher. It is an alloy of Cu-Sn.

**SUMMARY**

It is a binary alloy of Cu-Sn with a dendritic structure. The bulk composition conducted by AAS is 77.6% Cu and 17.8% Sn. Redeposited Cu bands are present in δ-removal areas and cracks in the metal.

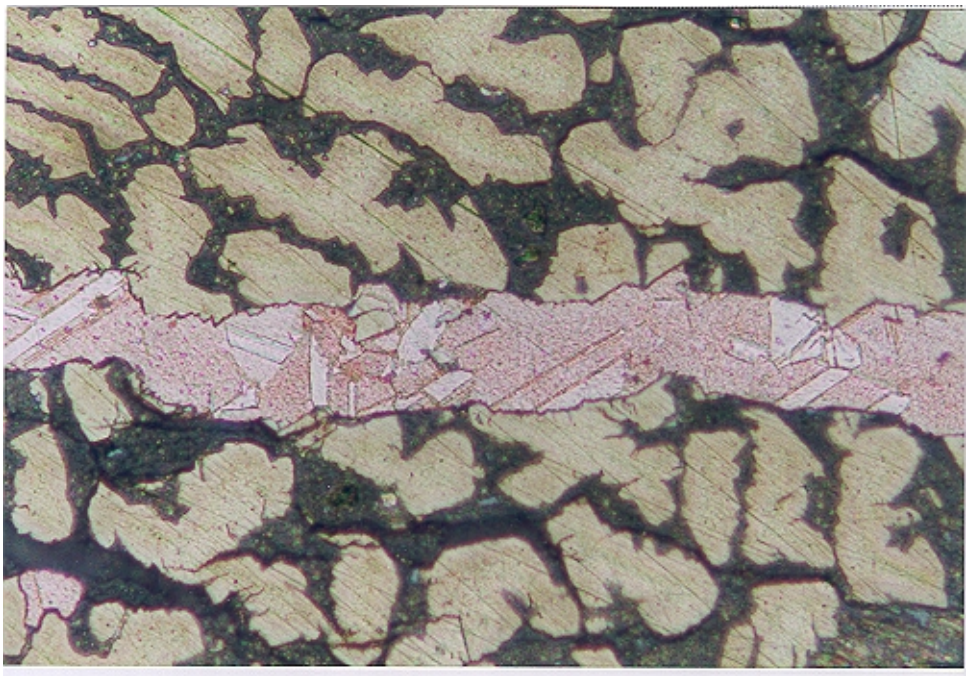


Fig. 5 Twinned structure of redeposited Cu. Etched in aqueous $FeCl_3$.

BF. Width of the image = 0.2 mm.

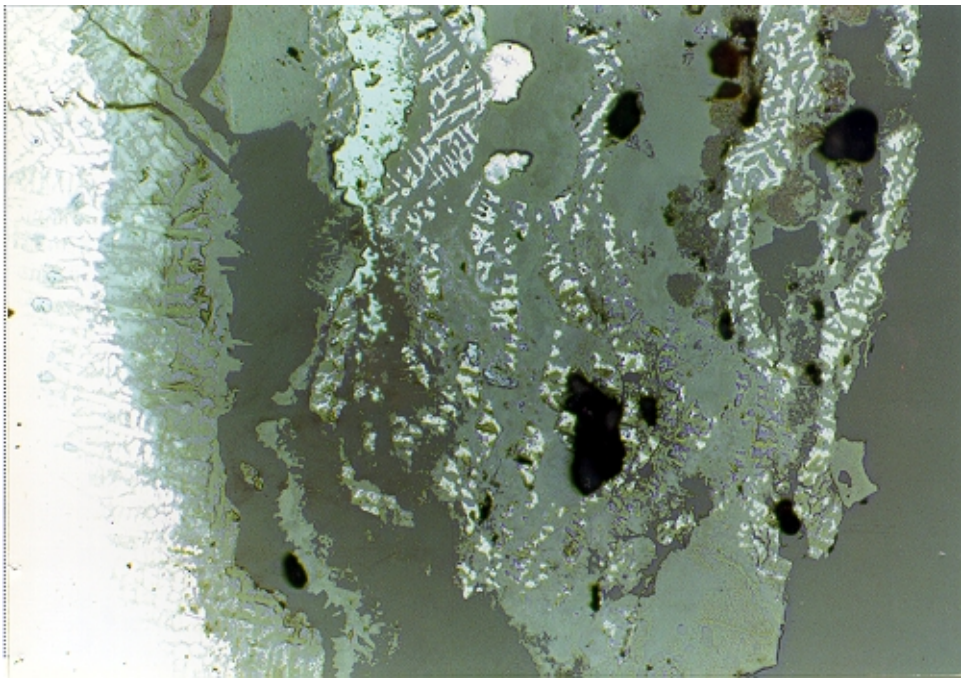


Fig. 6 Photomicrograph of corrosion with cracks.
BF. Width of the image = 1.4 mm.

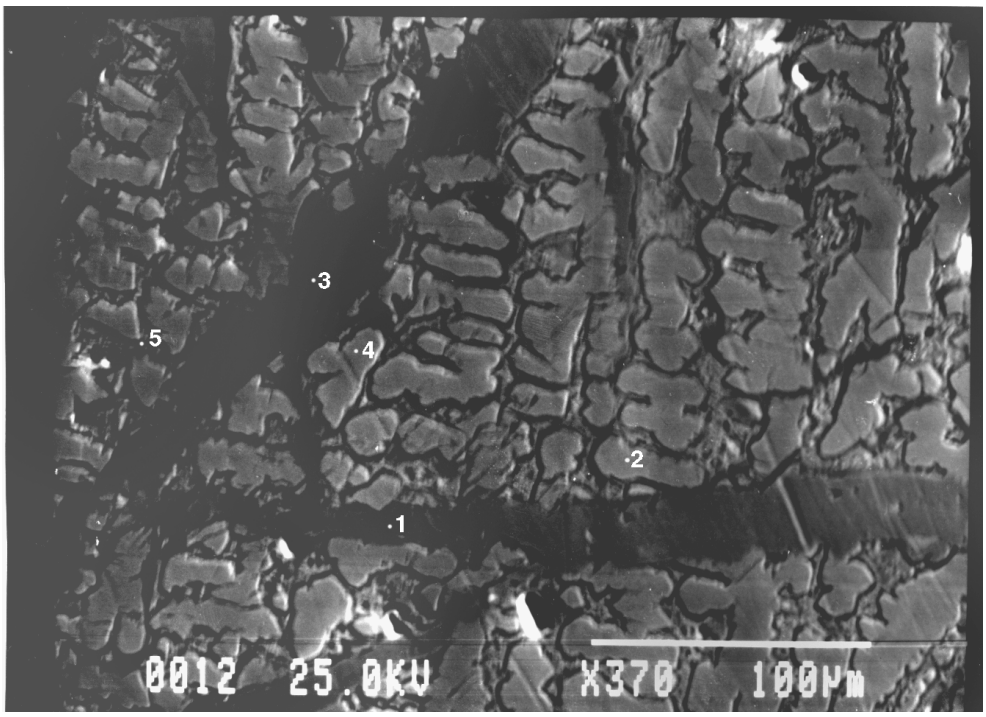



Fig. 7 SEI of metal, showing redeposited Cu bands and EPMA points.

## GENERAL

**Object Number:** M33:unknown3

**Object:** unknown

**Excavation Date:** 1994

**Date:** Late Western Zhou

**Origin:** Tianma-Qucun site

**Fragment Weight:** 35.9 g

**Fragment size:** 62x48x1.6 mm

**General description:**

This fragment has all sides broken. Metal remains in the middle. Corrosion index is 3. There is a thick corrosion overburdens on the surface. Corrosion products are light blue, black, brown, and green. Fibrous corrosion products and soil are also observed. No decoration is apparent (Fig. 1).

## TECHNICAL STUDIES OF METAL

**Metallographic structure:**

A section cut through full width of the fragment was taken for metallographic observation. The estimated original thickness is 1.6 mm as measured in the metallographic section. The original surfaces are disrupted; corrosion has gone all the way through the metal in some parts of the polished section. The metal has an equi-axed grain structure as seen in the corroded part (Fig. 2).

**Composition:**

**AAS:**

| Cu | Sn | Pb | Fe | As | Co | Zn | Ni | Ag | Au | Sb | Bi | total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ( | wt% | | ) | ( | | | ppm | | | | ) | (wt%) |
| 79.79 | 13.06 | 1.91 | 1.06 | 2850 | nd | 699 | 130 | 777 | nd | nd | nd | 96.27 |

**Microanalysis:**

Microprobe analysis was carried out on the metal, the result is as follows:

| Point | Cu | Fe | Sn | Pb | As | S | Cl | Total | Description |
|---|---|---|---|---|---|---|---|---|---|
| **1** | 85.34 | 0.03 | 15.23 | 0.08 | 0.00 | 0.00 | 0.00 | 100.68 | $\alpha$ phase |
| **2** | 10.58 | 0.07 | 0.05 | 61.82 | 0.60 | 7.63 | 0.12 | 80.86 | Lead |
| **3** | 15.29 | 0.21 | 0.08 | 85.00 | 0.00 | 0.00 | 0.00 | 100.40 | Lead |

It is hard to say whether metallic Pb was deliberately added or as an impurity.

**Microhardness:** 96Hv


Fig.1 General view of the fragment.

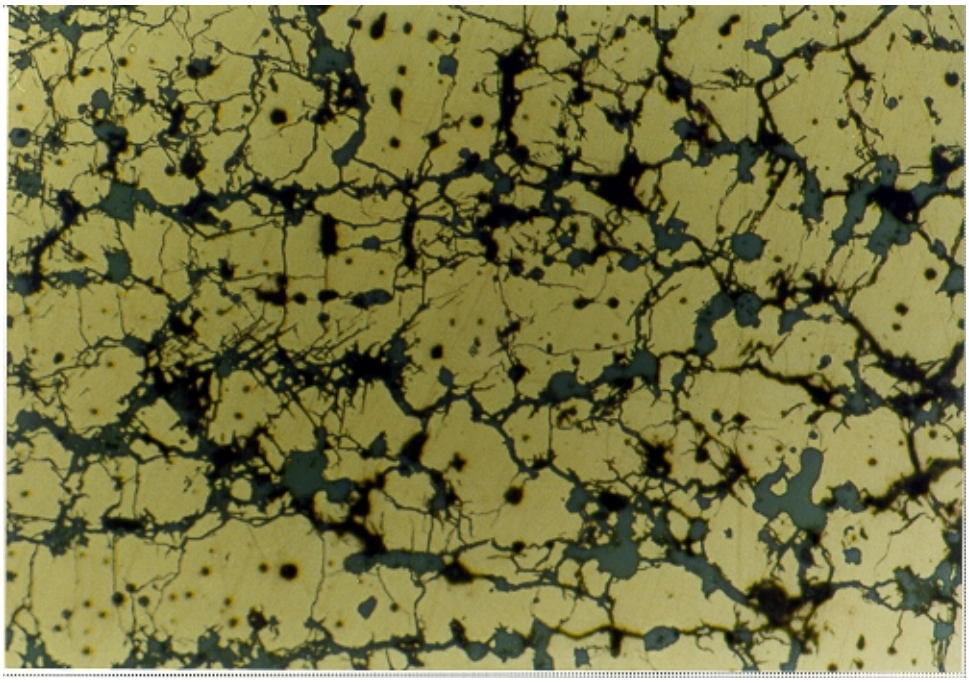


Fig. 2 Microstructure of corroded metal.

BF. Width of the image = 0.57mm.

## CORROSION

### XRD results:

Surface sample: Azurite, malachite, quartz, cassiterite, cuprite.

### Metallographic observation:

Corrosion follows grain boundaries (Fig. 2). A crack at an edge goes all the way through metal. Redeposited Cu is seen in the crack. Slip lines are observed on the surface (Fig. 3). They are probably the result of crystallographic corrosion.

### Microanalysis:

SEM analysis shows that Pb is rich in the outmost corrosion layers. Lead compounds are not evident by XRD due to the low concentration in the bulk metal.

## SUMMARY

The bulk composition conducted by AAS is 79.8% Cu, 13.1% Sn and 1.9% Pb. It is hard to say whether it is a binary or a ternary alloy due to its low AAS total as discussed in the entry of M33:unknown1. This sample has relatively high content of As. It is an equi-axed structure. Redeposited Cu is present in the cracks. This fragment could be from a vessel wall or base based on its flat shape.

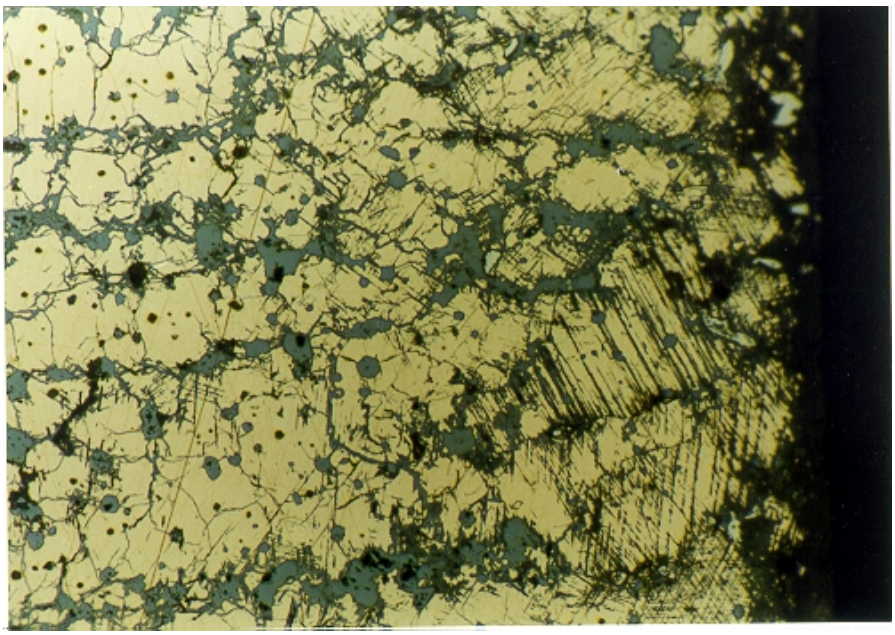


Fig. 3 Photomicrograph of redeposited Cu in a crack. BF. Width of the image = 0.57 mm.

**GENERAL**

**Object Number:** M33:unknown4

**Excavation Date:** 1994

**Origin:** Tianma-Qucun site

**Object:** horse fitting/snaffle bit

**Date:** Late Western Zhou

**Fragment Weight:** 31.7 g

**Fragment size:** 88x28 mm

5.8 mm thick in diameter

**General description:**

The entire object is supposed to be like the one shown in Fig. 1 Therefore, this fragment is almost half of the entire object. It is broken at 2 ends. There is sound metal in the middle. Corrosion index is 2. There is a thick corrosion overburden and soil on the surface. Corrosion products are light blue, light green and red. Fibrous corrosion is also observed. No decoration is apparent (Fig. 2)

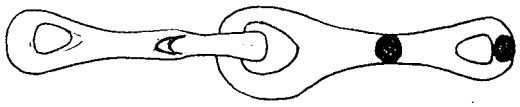


Fig. 1 Schematic representation of a horse fitting / snaffle bit.


Fig. 2 General view of the fragment. Section cut from upper right of broken loop.

## TECHNICAL STUDIES OF METAL

### Metallographic structure:

A section cut through the whole thickness at the broken edge on the right of Fig. 2 was taken for metallographic observation. The shape of the cross section is odd (Fig. 3). It does not seem to have been cast in bivalve moulds. However, there is no evidence of hammering. It could be due to a specific mould construction. The estimated diameter is 5.8 mm as measured in the metallographic section. It has a dendritic structure (Fig. 4).

### Composition:

**AAS:**

| **Cu** | **Sn** | **Pb** | **Fe** | **As** | **Co** | **Zn** | **Ni** | **Ag** | **Au** | **Sb** | **Bi** | **total** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ( | wt% | | ) | ( | | | ppm | | | | ) | (wt%) |
| 80.24 | 9.01 | 1.15 | 0.93 | nd | 202 | 766 | 403 | 403 | nd | nd | nd | 91.51 |

**Microanalysis:**

Colour maps have been carried out on an area of metal (Fig .5) to see the distribution of As (because EPMA point analysis of point1 shows 7.7 %As). It is shown in Fig. 6. Lead inclusions are present in eutectoid. Arsenic seems to have correlation with Pb. Arsenic is not detected by AAS due to a very low concentration in the bulk metal.

**Microhardness:** 145Hv

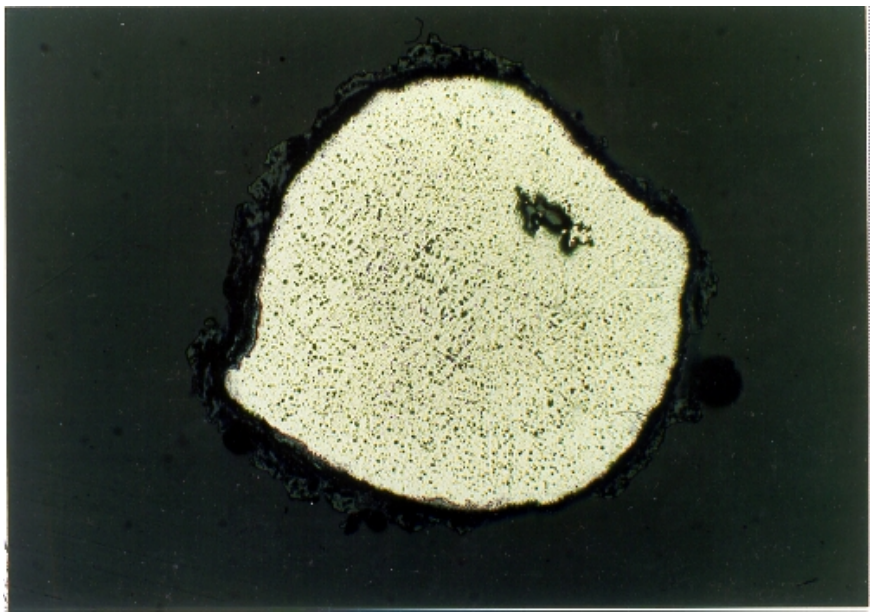


Fig. 3 Metallographic section. The estimated diameter = 5.8 mm.

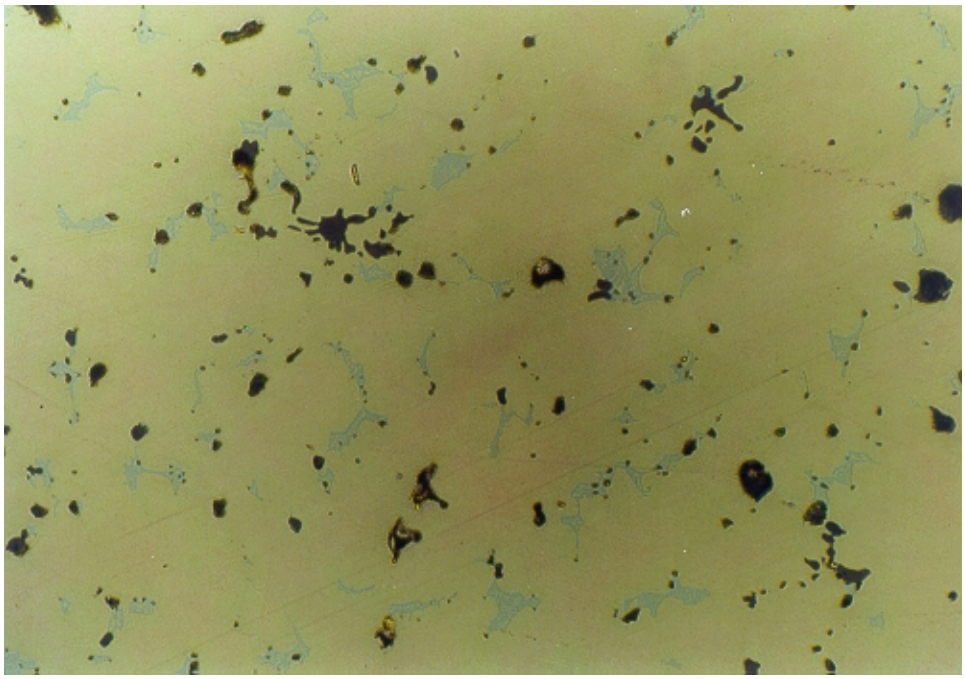


Fig. 4 Dendritic microstructure.

BF. Width of the mage = 0.28 mm.

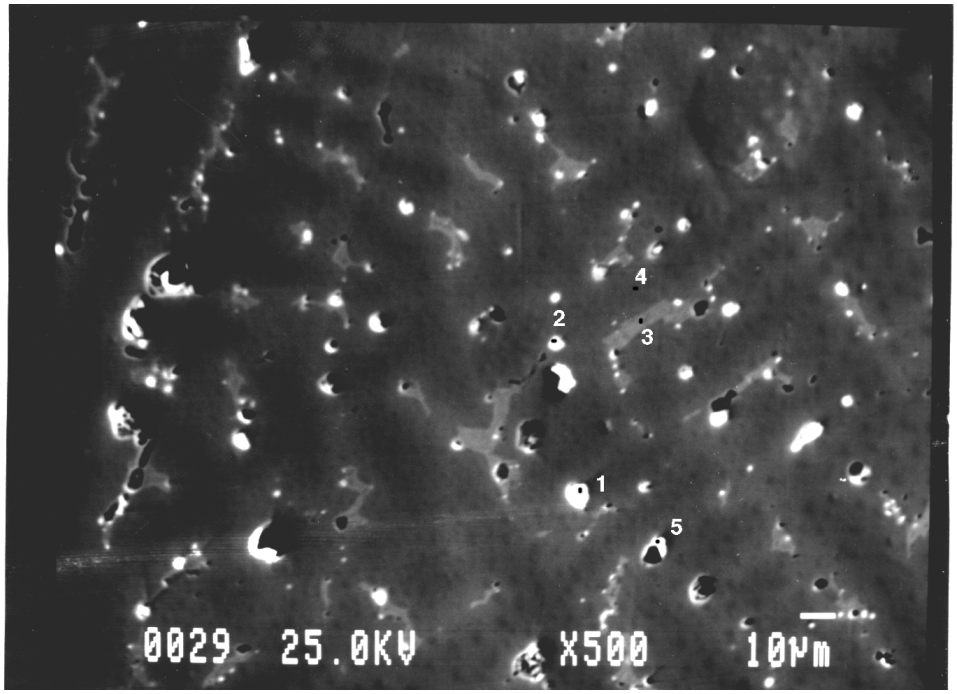



Fig. 5 SEI of metal, showing EPMA points. Colour map has been done on this area .

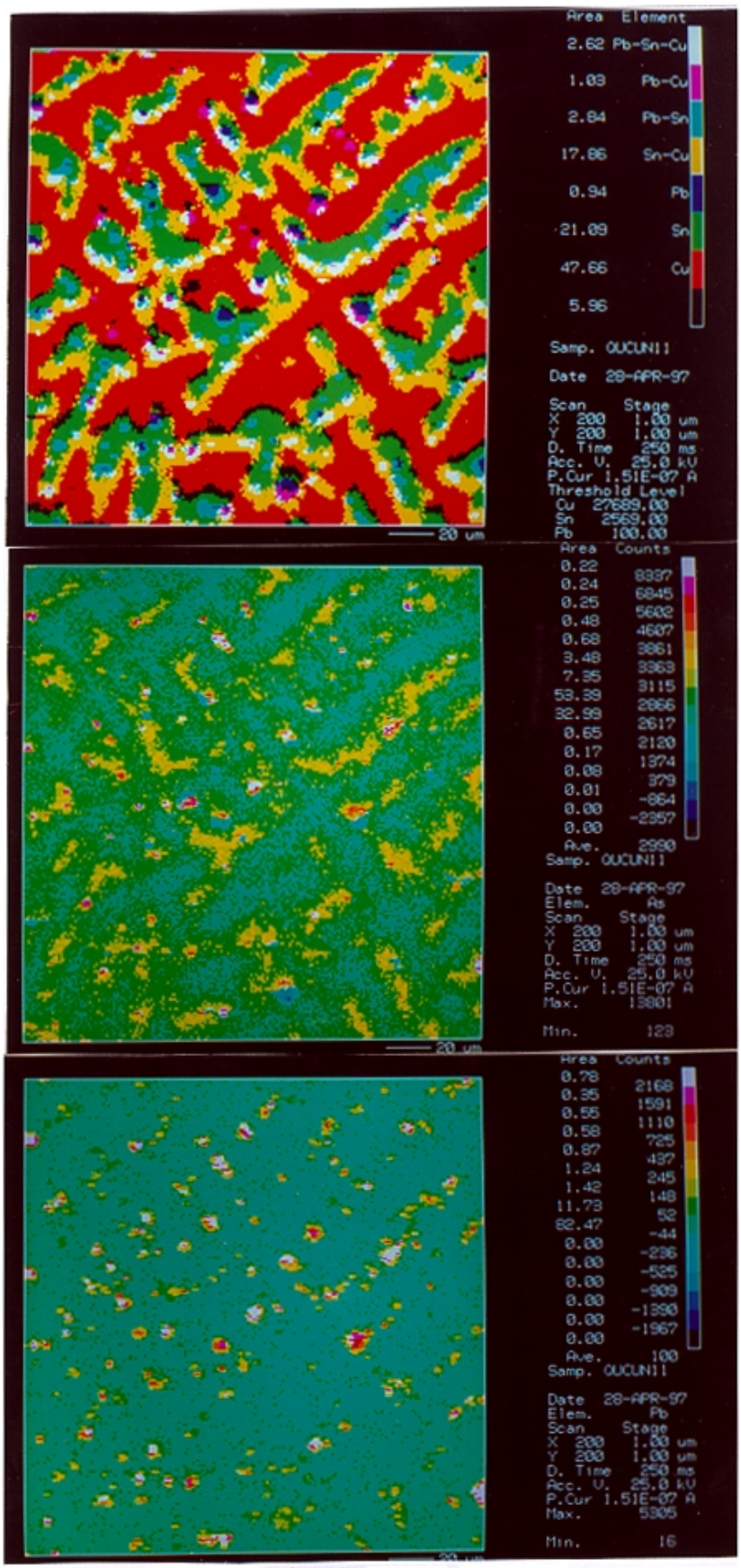



Fig. 6 Colour maps of elemental distribution, showing inclusions of Pb and As in some areas.

## CORROSION

### XRD results:

Surface sample: malachite, azurite, cuprite, cassiterite, $Pb_3O_2SO_4$, brochantite?

### Metallographic observation:

δ phase is corroded away in some areas of the metal core. On the surface, corrosion apparently developed along the slip lines (Fig. 7). Based on their characteristic colours in the metallographic section and microprobe analysis (see below), corrosion products are cuprite mixed with cassiterite on the original surface, and copper sulphide in the outermost layer.

### Microanalysis:

Microprobe analyses were carried out on both metal (Fig. 5) and corrosion (Fig. 8); the results are as follow:

| Point | Cu | Fe | Sn | Pb | As | S | Cl | Total | Description |
|---|---|---|---|---|---|---|---|---|---|
| **1** | 37.00 | 0.51 | 6.76 | 48.86 | 7.69 | 0.15 | 0.38 | 101.34 | Lead grain |
| **2** | 36.10 | 1.15 | 10.96 | 52.09 | 0.00 | 0.00 | 0.01 | 100.30 | Lead grain |
| **3** | 68.68 | 0.25 | 28.00 | 1.46 | 0.00 | 0.00 | 0.00 | 98.39 | Eutectoid |
| **4** | 87.65 | 1.39 | 9.23 | 0.11 | 0.00 | 0.02 | 0.00 | 98.39 | α phase |
| **5** | 21.65 | 1.01 | 5.25 | 61.94 | 0.00 | 1.96 | 0.00 | 91.80 | Lead grain |
| **6** | 77.58 | 0.01 | 0.00 | 0.02 | 0.00 | 19.28 | 0.01 | 96.89 | Copper sulphide |
| **7** | 47.27 | 1.37 | 38.87 | 2.42 | 0.00 | 0.05 | 0.04 | 90.00 | Mixed corrosion |
| **8** | 84.65 | 0.02 | 0.05 | 0.00 | 0.00 | 0.00 | 0.23 | 84.95 | Cuprite |
| **9** | 66.05 | 1.07 | 10.81 | 1.36 | 0.00 | 0.02 | 1.40 | 80.72 | Mixed corrosion |

## SUMMARY

It is a binary alloy of Cu-Sn with a dendritic structure. The bulk composition conducted by AAS is 80.2% Cu, 9.0% Sn and 1.2% Pb. Corrosion developed along slip lines. Lead is as an impurity rather than deliberately added. Arsenic inclusions are observed using EPMA, but not detected by AAS due to its low concentration in the bulk metal.

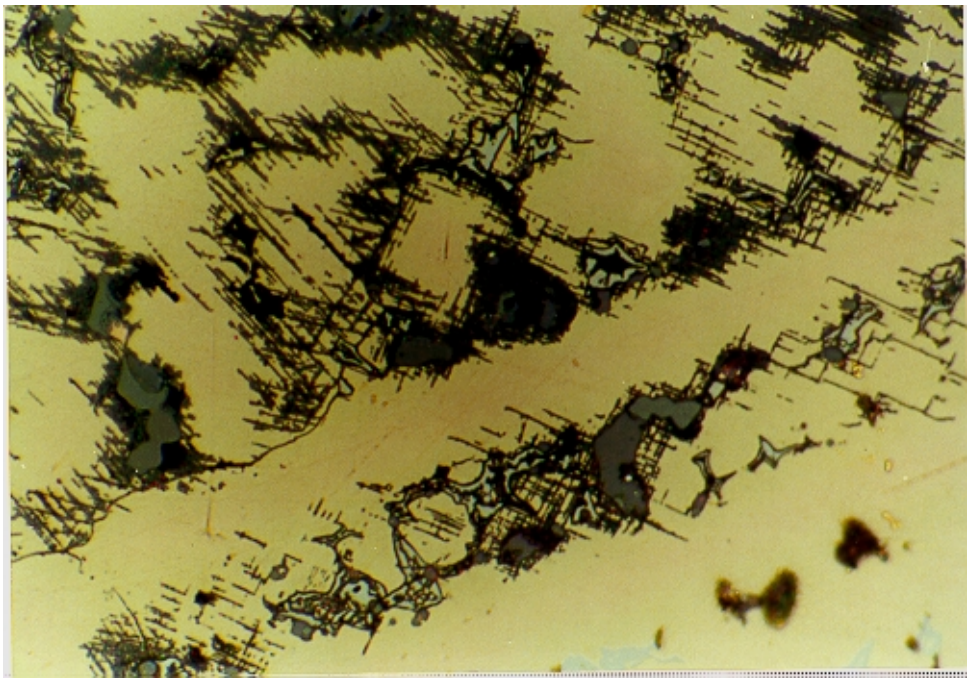


Fig. 7 Photomicrograph showing corrosion developing along slip lines.
BF. Width of the image = 0.14 mm.

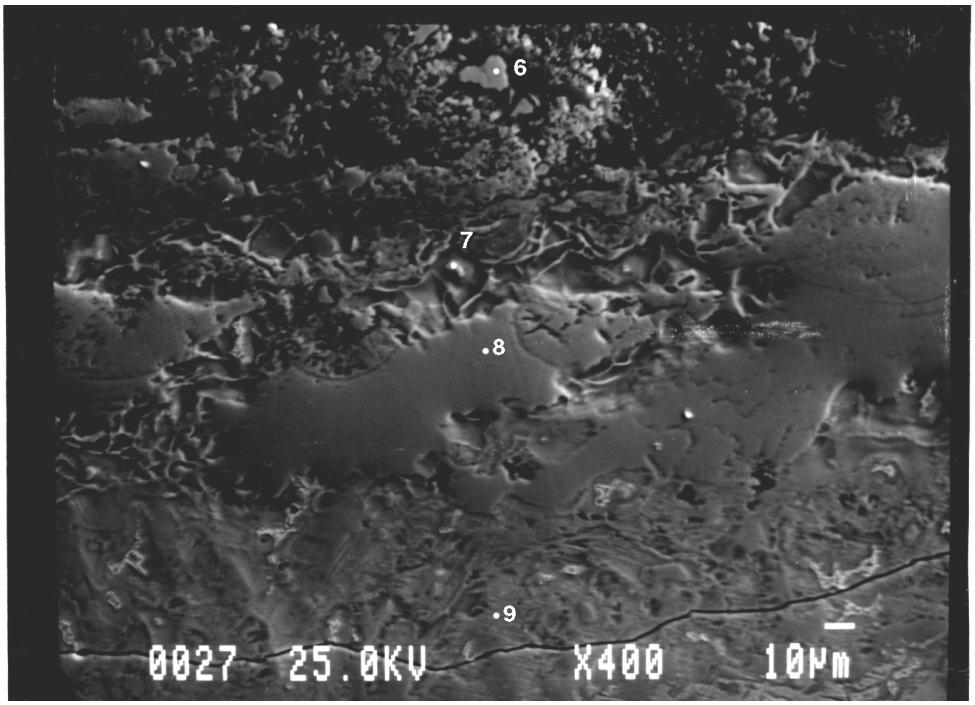



Fig. 8 SEI of corrosion, showing EPMA points.

## GENERAL

**Object Number:** M91:137A
**Excavation Date:** 1994
**Origin:** Tianma-Qucun site

**Object:** Vessel/*ding*
**Date:** Late Western Zhou
**Fragment Weight:** 10.2 g
**Fragment size:** 28x11x4.5 mm

**General description:**

This fragment has all sides broken. Corrosion index is 3. There is a thin corrosion overburden. The surface is covered with corrosion products and soil. The corrosion products are mainly light green and black materials, with the black one being the majority. No decoration is apparent (Fig. 1). Holes filled with cuprite (red shinning material) or lead compounds (white powdery material) are seen on the fresh cut surface (Fig. 2).

## TECHNICAL STUDIES OF METAL

**Metallographic structure:**

A section cut through the full width of the fragment was taken for metallographic observation. The estimated original thickness is 4.5 mm as measured in the metallographic section. It has an equi-axed grain structure (Fig. 3). The average grain size is 0.040 mm. Light blue (in BF) grains with round, square or polygonal shapes are seen in α grains (Fig. 4). EPMA shows that they contain Fe (see below). The holes are filled with cuprite surrounded by a thin ring of copper sulphide. A void with very sharp edge is seen in each of holes, which seems resulted from a crystalline material missing (Fig. 3). No evidence of annealing twins is seen, therefore, equi-axed structure assumes this object was cooled slowly.

**Composition:**

**AAS:**

| **Cu** | **Sn** | **Pb** | **Fe** | **As** | **Co** | **Zn** | **Ni** | **Ag** | **Au** | **Sb** | **Bi** | **total** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ( | wt% | | ) | ( | | | ppm | | | | ) | (wt%) |
| 75.60 | 10.31 | 0.436 | 0.720 | nd | nd | 300 | 100 | 400 | nd | nd | nd | 87.15 |

The low total is due to corrosion.

**Microanalysis:**

See corrosion section.

**Microhardness:** 120Hv

Fig. 1 General view of the fragment. Length of the fragment = 28 mm.

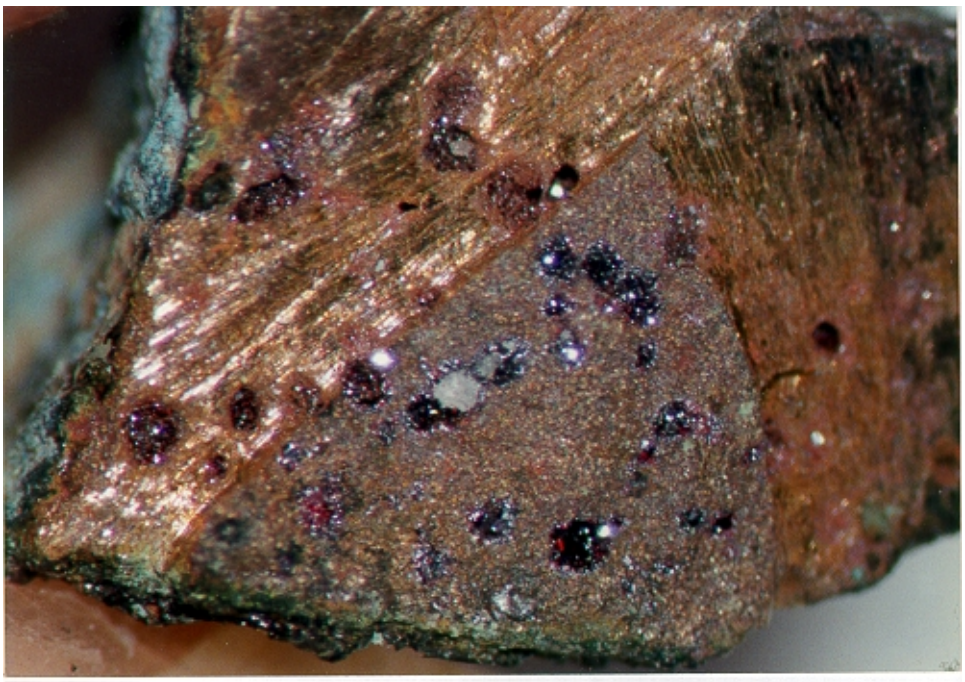


Fig. 2 Cross section of cut off piece, showing cerussite in the holes of cuprite.

Width of the image = 8 mm.

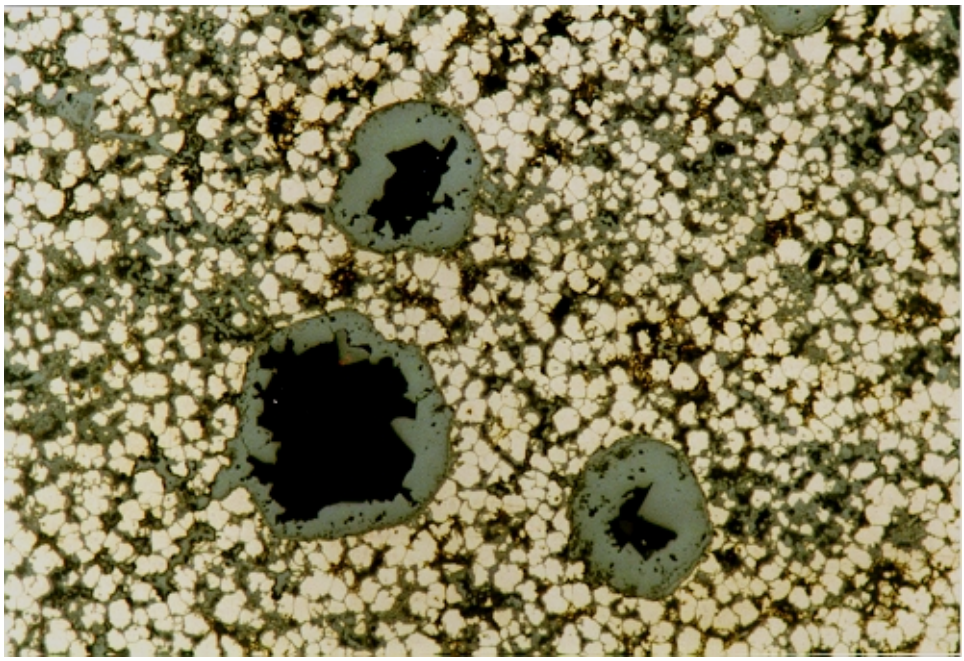


Fig. 3 Photomicrograph of big holes filled with cuprite in the metal.

BF. Width of the image = 2mm.

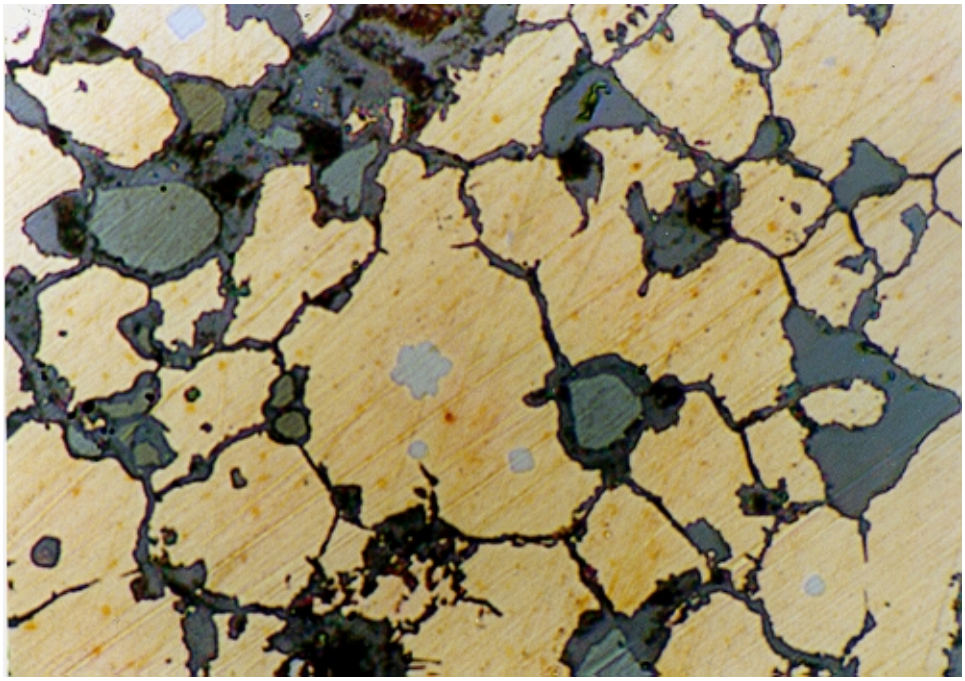


Fig. 4 Photomicrograph of metallic Fe inclusion in α grains.

BF. Width of the image = 0.15 mm.

## CORROSION

### XRD results:

Surface sample: cuprite, cassiterite, lead sulphate ($PbSO_3$).

Black materials from inner layer of corrosion: cuprite, lepidocrocite [FeO(OH)], maghemite ($Fe_2O_3$), malachite, azurite, humboldtine ($C_2FeO_4.2H_2O$), $Fe_2CuO_4$(?) $Fe_2(SO_4)_3.11H_2O$(?)

### Metallographic observation:

Corrosion overburdens are thin on both original surfaces. One of the original surfaces is well preserved, while the other one is not very clear. Redeposited Cu is seen within cuprite on grain boundaries (Fig. 5). A banded layer is formed on the surface running all the way around the whole piece. The banded layer is grey colour in bright field, and appears yellow- brown - black colour in cross polars (Fig. 6). Inside the metal, corrosion follows grain boundaries. The holes are partially filled with cuprite, and occasionally lead. They are probably the result of the replacement of lead, i.e. the original lead inclusions have corroded to form lead compounds (probably $PbSO_3$ based on XRD result and EPMA data), which are in turn replaced by cuprite and copper sulphide.

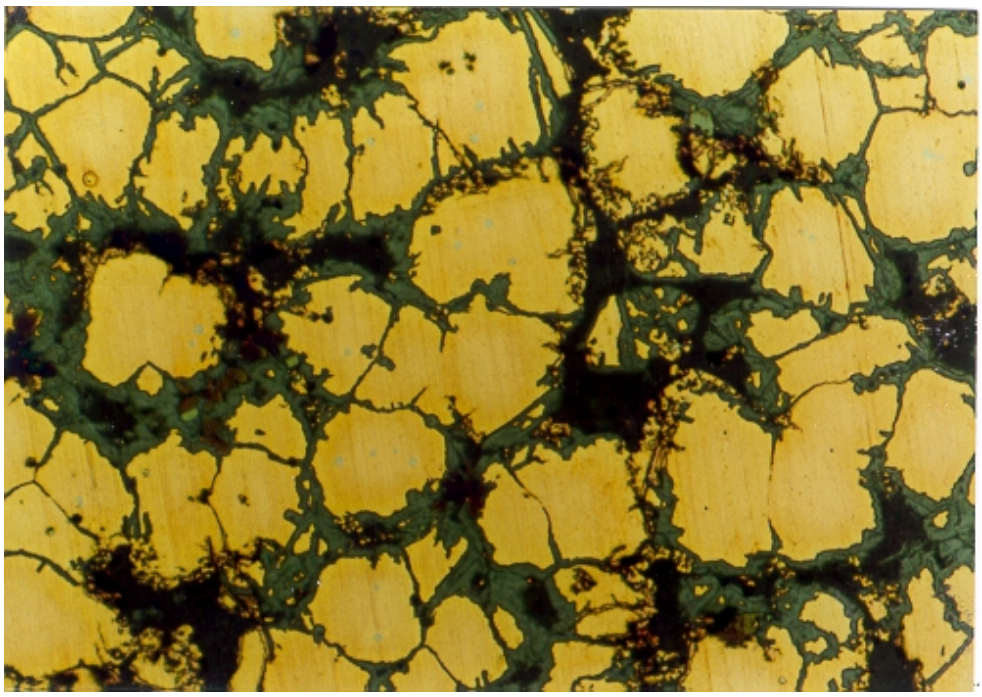


Fig. 5 Photomicrograph of corroded metal, showing redeposited Cu on grain boundaries. BF. Width of the image = 0.7 mm.

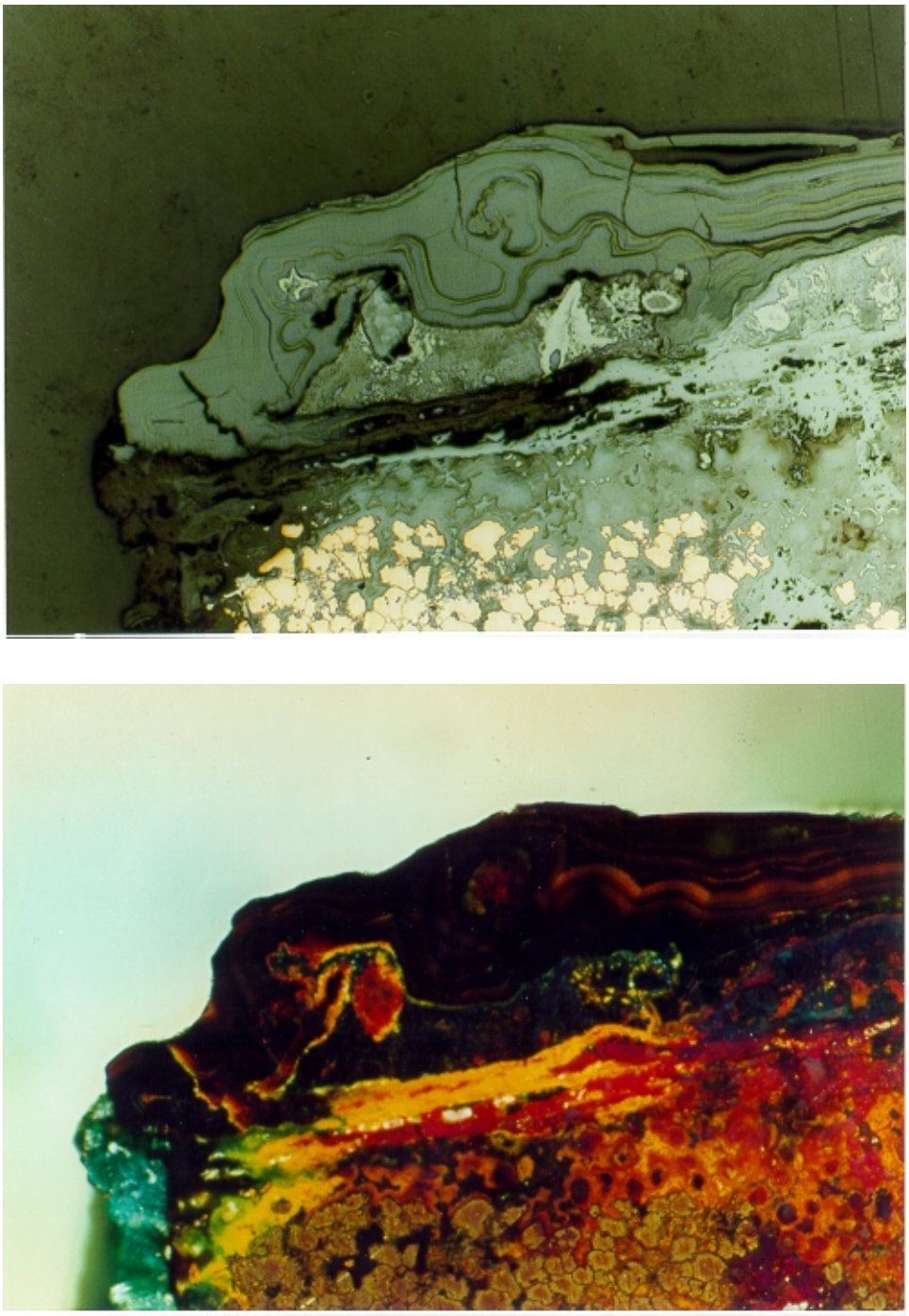


Fig. 6  Photomicrograph of banded Fe corrosion on the surface.

Top: BF. Bottom: C/P

Width of the image = 4 mm.

**Microanalysis:**

EPMA was carried out on an area with holes (Fig. 7) and the banded corrosion layer (Fig. 8); the results are listed below. Lead is evident in the backscattered electron image in some holes (Fig. 7).

| Point | Description |
|---|---|
| **1** | α grain |
| **2** | Edge of α grain |
| **3** | Cuprite |
| **4** | Lead corrosion |
| **5** | Lead corrosion |
| **6** | Fe in α grain |
| **7** | Banded corrosion |
| **8** | Brighter line (under optical microscope) in the banded corrosion |
| **9** | Beneath banded corrosion |
| **10** | α grain |
| **11** | Corroded α grain |

| Point | Cu | Ni | Fe | Sn | Pb | As | Zn | Co | S | Cl | total |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 88.93 | 0.00 | 1.14 | 8.93 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 99.00 |
| **2** | 83.50 | 0.02 | 1.48 | 10.31 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 95.32 |
| **3** | 83.33 | 0.00 | 0.00 | 0.02 | 0.10 | 0.00 | 0.00 | 0.00 | 0.00 | 0.19 | 84.65 |
| **4** | 0.99 | 0.00 | 0.04 | 0.02 | 67.93 | 0.00 | 0.00 | 0.00 | 9.92 | 0.02 | 78.93 |
| **5** | 16.35 | 0.01 | 0.05 | 0.00 | 20.65 | 1.17 | 0.00 | 0.04 | 4.62 | 0.01 | 42.90 |
| **6** | 11.21 | 0.09 | 80.85 | 0.54 | 0.05 | 0.00 | 0.00 | 0.23 | 0.15 | 0.19 | 93.29 |
| **7** | 9.23 | 0.00 | 39.60 | 0.01 | 0.16 | 0.00 | 0.00 | 0.02 | 0.35 | 0.02 | 49.38 |
| **8** | 12.40 | 0.01 | 39.85 | 0.00 | 0.14 | 0.00 | 0.00 | 0.04 | 0.21 | 0.05 | 52.70 |
| **9** | 61.15 | 0.00 | 4.79 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 2.78 | 1.06 | 69.79 |
| **10** | 89.64 | 0.01 | 1.44 | 5.95 | 0.06 | 0.00 | 0.00 | 0.02 | 0.02 | 0.00 | 97.14 |
| **11** | 54.56 | 0.00 | 1.84 | 16.21 | 0.34 | 0.00 | 0.00 | 0.00 | 0.18 | 0.40 | 73.52 |

Moreover, colour maps have been carried out on the banded corrosion layer (Fig. 9). It shows the enrichment of Fe in the banded corrosion. The banded corrosion is likely a mixture of cuprite and iron oxide or/and iron hydroxide. This determination is based on XRD and EPMA data.

## SUMMARY

It is a binary alloy of Cu-Sn with an equi-axed structure. The best estimate of the original tin content determined by AAS is about 10%. Random presence of lead suggests an impurity rather than deliberately addition. Minor element Fe is relatively high. Holes filled with cuprite, Pb or cerrucite are present inside the metal, which

were originally Pb but corroded and replaced by cuprite. Fe enriched corrosion bands are seen on the surface due to accumulation of Fe from soil and corrosion of Fe from the metal.

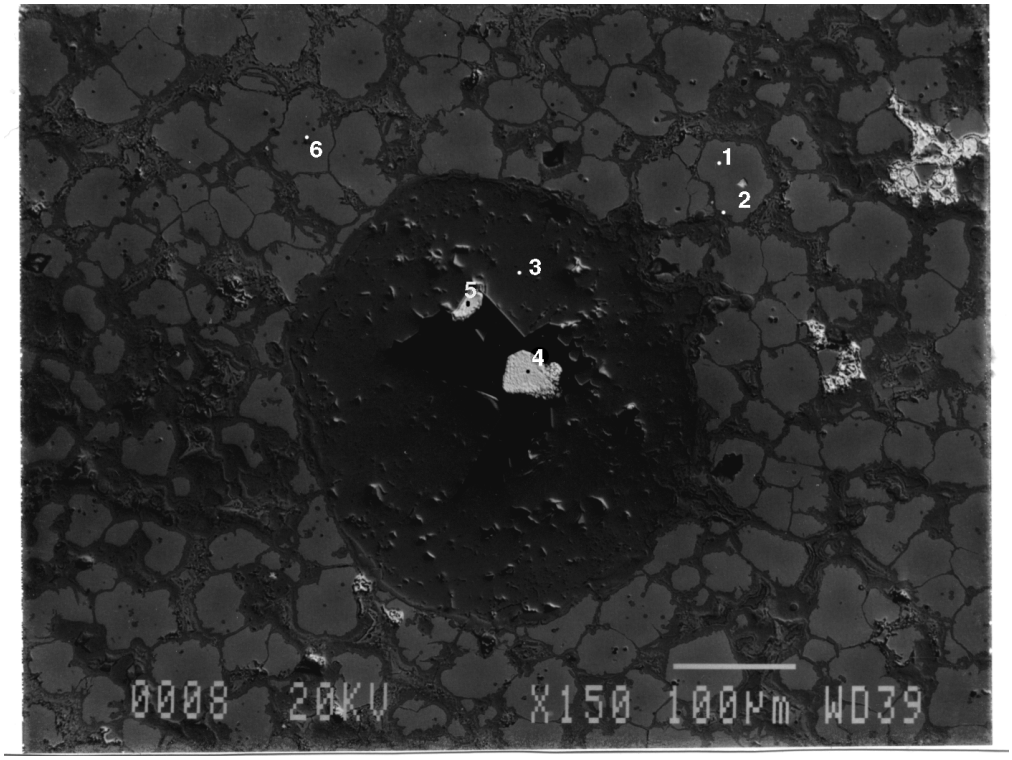



Fig. 7 BEI of a big hole with Pb and $Cu_2O$, showing EPMA points.

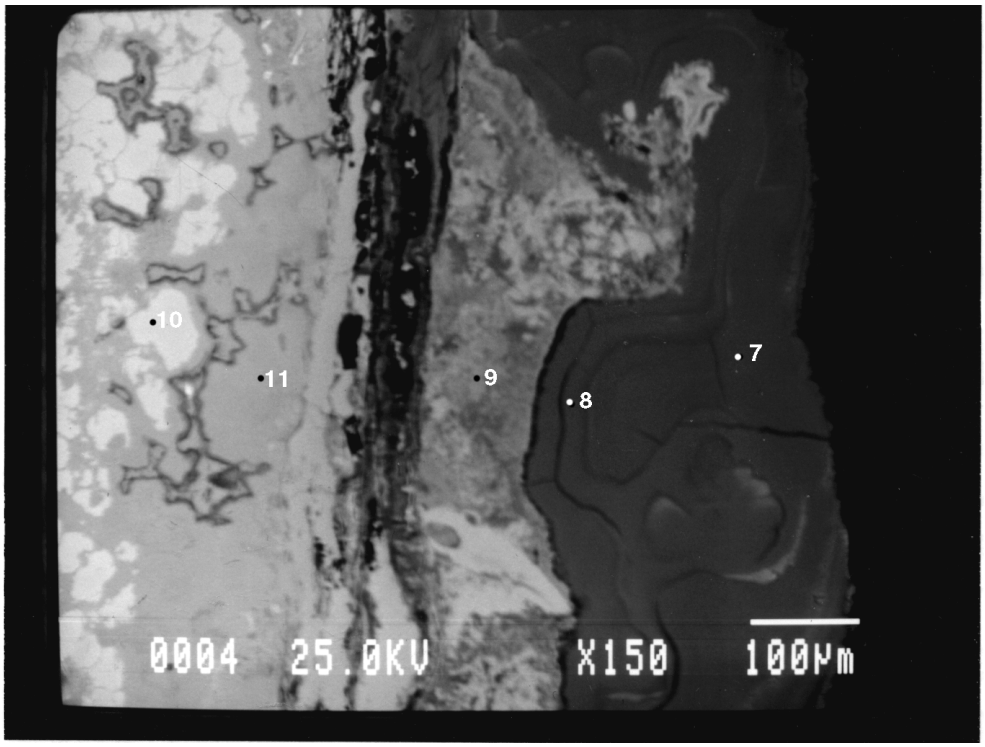



Fig. 8 BEI of a banded Fe corrosion, showing EPMA points.

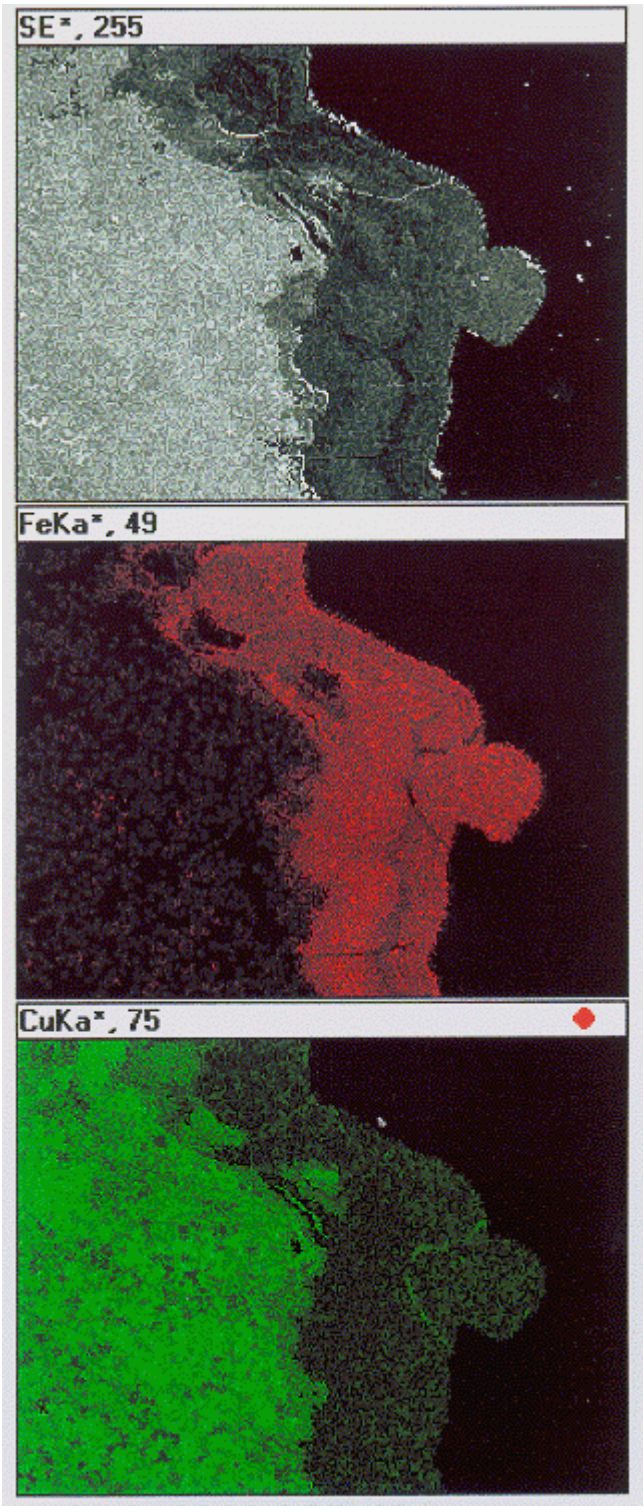



Fig. 9 SEM/EDS colour maps of the banded corrosion layer (on the right). 100X

## GENERAL

**Object Number:** M91:137B
**Excavation Date:** 1994
**Origin:** Tianma-Qucun site

**Object:** Vessel/*ding*
**Date:** Late Western Zhou
**Fragment Weight:** 3.6 g
**Fragment size:** 12x 9x? mm

**General description:**

It is a fragment thought to be from the same object as M91:137A by the excavators. It looks like a piece of corrosion product rather than metal, very light and porous. Corrosion includes blue, grey and red materials and soil. A layer of light green material is sandwiched between blue and grey corrosion products (Fig. 1)

## TECHNICAL STUDIES OF METAL

**Metallographic structure:**

A section cut through the full width of the fragment was taken for metallographic observation. The original thickness is hard to estimate due to its unclear structure. The original metal seems to be the light green part sandwiched in the middle, since δ-remains are present (Fig. 2).

**Composition:**

**AAS:** too corroded for analysis.

**Microanalysis:**

SEM/EDS semi-quantitative analysis was carried out on the green part (100x) and the surrounding grey part (100x); the results are shown below:

Green part in the middle:

| Cu | Sn | Pb | Fe | As | P | Si | Total |
|---|---|---|---|---|---|---|---|
| 4.1 | 32.5 | 11.9 | 3.5 | 0.9 | 0.4 | 0.9 | 54.3 |

Grey part surrounding the green part:

| Cu | Sn | Fe | Ca | S | Total |
|---|---|---|---|---|---|
| 33.4 | 3.7 | 0.3 | 0.3 | 0.8 | 38.5 |

This just gives one the idea that the original metal was a leaded bronze. Moreover, the composition of the corrosion seems to be mainly copper compounds. The very low total is due to the porous nature of this sample.

**Microhardness:** too corroded for measuring

Fig. 1 General view of the fragment. Diameter of this piece ≈ 10 mm.

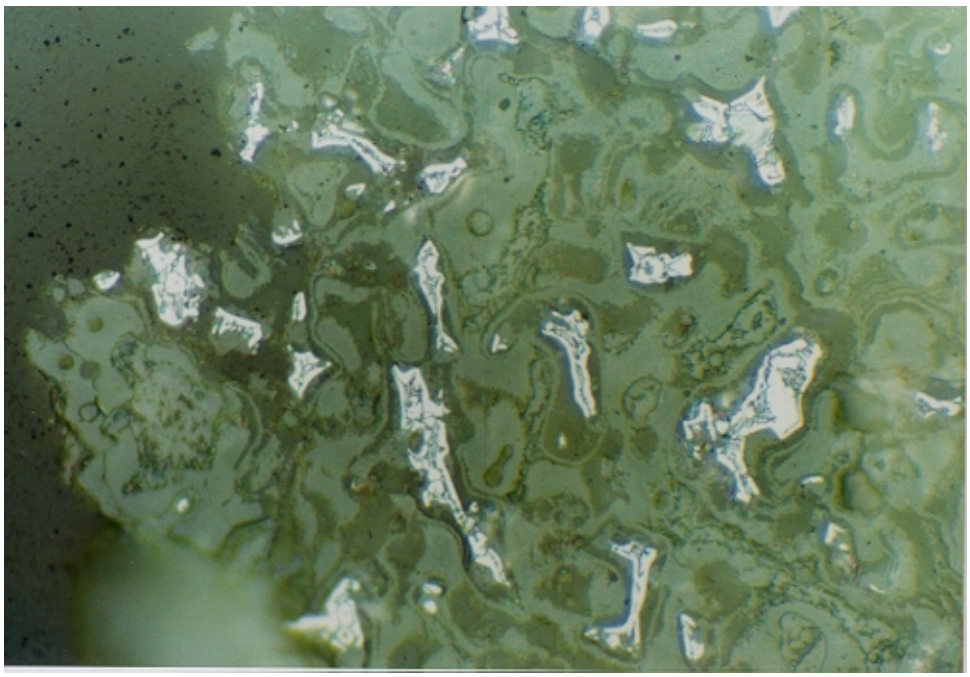


Fig. 2 Photomicrograph of δ remains in the green part in the middle of the fragment. BF. Width of the image = 0.15 mm.

## CORROSION

**XRD results:** not carried out.

**Metallographic observation:**

The light green part with δ-remains is 1.9 mm thick, the corrosion overburden on both sides is up to 4.1 mm thick. Azurite, malachite, including the fibrous type, cuprite and cassiterite are present in the corrosion overburden based on their characteristic colours in the metallographic section (Fig. 3). There also are many copper sulphide crystals with fractures in corrosion overburden.

**Microanalysis:**

EPMA spot analyses were carried out on both light green part in the middle and the corrosion overburden (Figs. 4 & 5), the results are as follow. Arsenic is measured in the grey part (overburden), and seems to be related with copper sulphides. The source of arsenic must have been from the burial environment. This is discussed in Chapter 6.

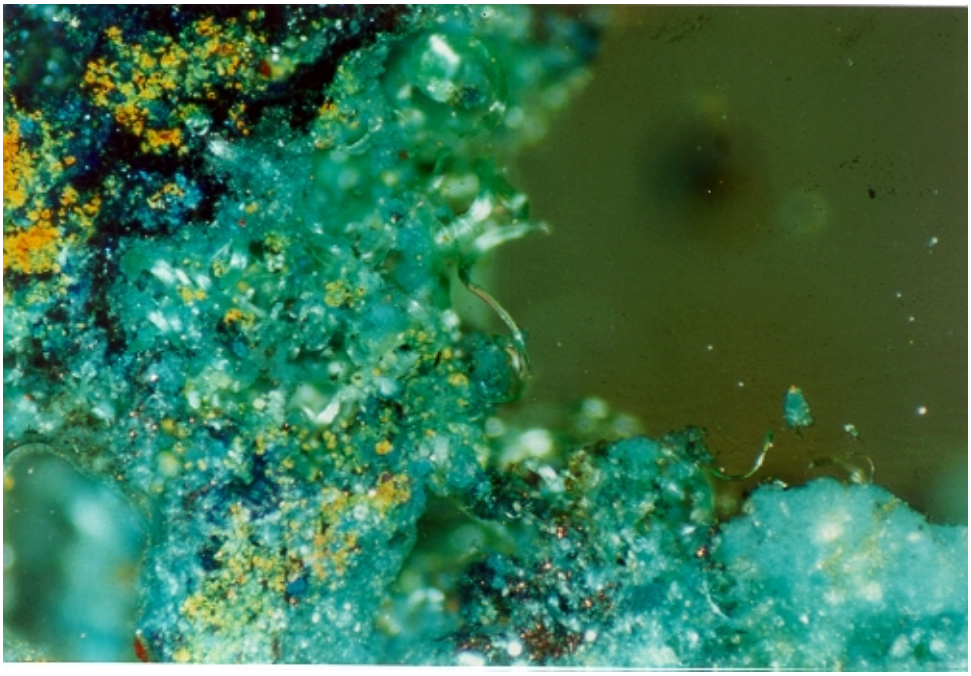


Fig. 3 Photomicrograph of corrosion products. C/P. Width of the image = 1.5mm.

| Point | Description |
|---|---|
| **1, 4** | Lead corrosion in green part |
| **2, 3** | Corroded matrix in green part |
| **5, 10** | Copper carbonates in grey part |
| **6, 7, 8, 11** | Copper sulphides |
| **9** | Hole |

| point | Cu | Fe | Sn | Pb | S | Cl | Ag | Bi | As | Total |
|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 0.65 | 0.26 | 2.16 | 67.53 | 0.00 | 0.06 | 0.00 | 0.00 | 0.00 | 70.65 |
| **2** | 5.71 | 5.62 | 36.01 | 9.76 | 0.00 | 0.02 | 0.00 | 0.27 | 0.00 | 57.39 |
| **3** | 8.11 | 5.96 | 41.66 | 7.96 | 0.00 | 0.00 | 0.00 | 0.23 | 0.00 | 63.93 |
| **4** | 0.51 | 0.16 | 0.59 | 73.82 | 0.00 | 0.04 | 0.00 | 0.00 | 0.00 | 75.11 |
| **5** | 48.59 | 0.03 | 0.03 | 0.27 | 0.20 | 0.00 | 0.00 | 0.07 | 0.00 | 49.18 |
| **6** | 59.07 | 0.00 | 0.02 | 0.00 | 15.88 | 0.00 | 0.31 | 0.17 | 5.94 | 81.39 |
| 7 | 56.01 | 0.00 | 0.00 | 0.00 | 18.99 | 0.00 | 0.14 | 0.06 | 1.41 | 76.60 |
| **8** | 65.62 | 0.01 | 0.00 | 0.00 | 22.10 | 0.00 | 0.21 | 0.19 | 3.81 | 91.94 |
| **9** | 0.60 | 0.00 | 0.01 | 0.02 | 0.11 | 0.15 | 0.00 | 0.03 | 0.18 | 1.10 |
| **10** | 48.85 | 0.00 | 0.00 | 0.01 | 1.47 | 0.00 | 0.12 | 0.04 | 0.00 | 50.50 |
| **11** | 51.22 | 0.00 | 0.01 | 0.03 | 21.91 | 0.00 | 0.09 | 0.06 | 6.42 | 79.74 |

## SUMMARY

It seems to be a ternary alloy of Cu-Sn-Pb with a dendritic structure. It is too badly corroded to estimate the original composition. The corrosion overburden is thick, mainly comprised of copper compounds. This piece is unlikely to be from the same object as M91:137A based on its composition and structure. If it was from the same object, it must have not been from the same part as M91:137A, i.e. they must have been made separately.

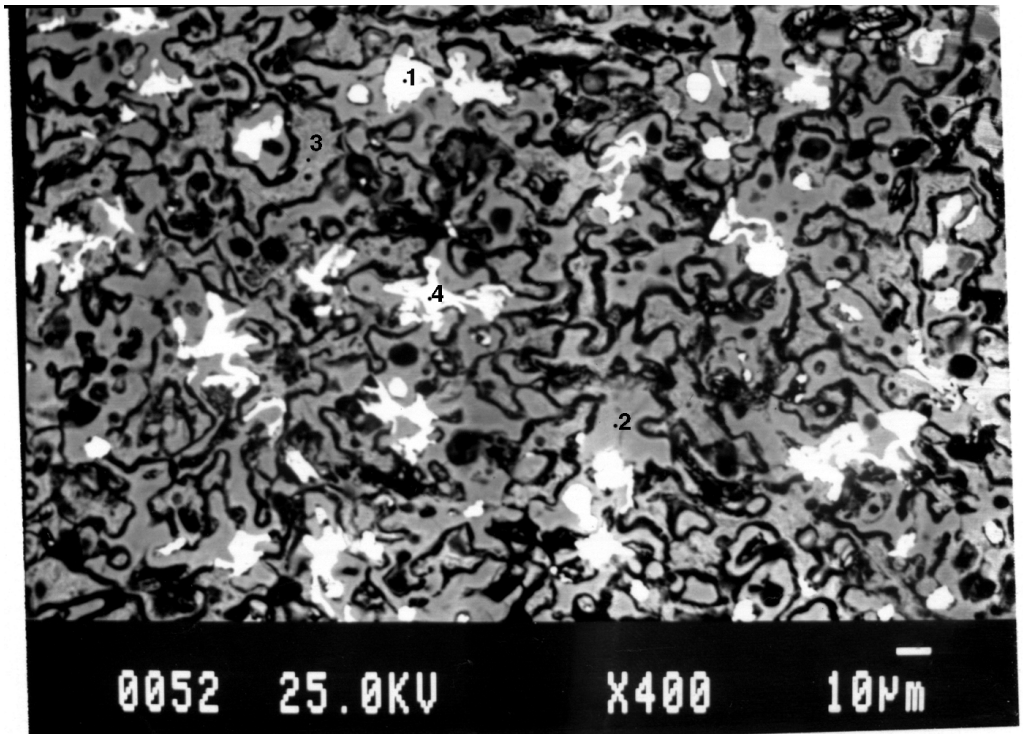



Fig. 4 BEI of corroded metal (green part), showing EPMA points.

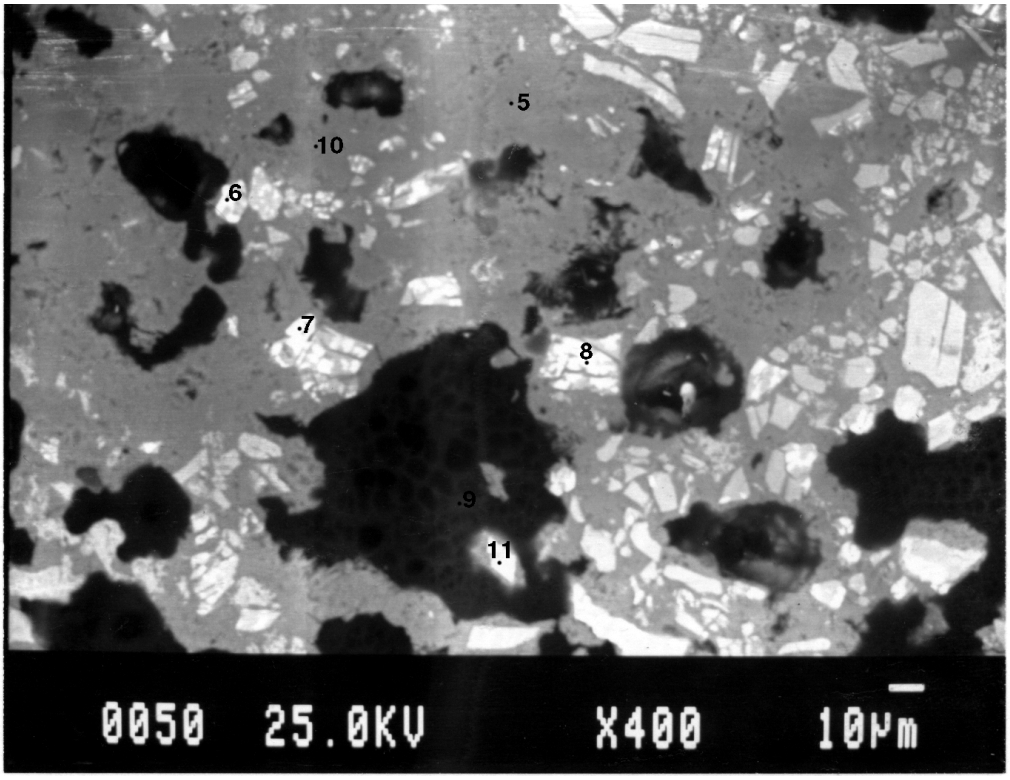



Fig. 5 BEI of corrosion overburden (grey part), showing EPMA points.

## GENERAL

**Object Number:** M91:139A
**Excavation Date:** 1994
**Origin:** Tianma-Qucun site
**Object:** Vessel/*ding*
**Date:** Late Western Zhou
**Fragment Weight:** 6.6 g
**Fragment size:** 28x20x2 mm

**General description:**

This fragment has all sides broken. Corrosion index is 3. There is a thick corrosion overburden. The surface is covered with corrosion products (Figs. 1 & 2), including green, red, brown and black ones. No decoration is apparent.

## TECHNICAL STUDIES OF METAL

**Metallographic structure:**

A metallographic section is shown in Fig. 3. The estimated original thickness is 2mm as measured in the metallographic section. It has an equi-axed structure (Figs. 4 & 5). The average grain size is 0.015 mm. The backscattered electron image (Fig. 6) shows very few δ phases are present (brighter needle or dendrite). Sulphide inclusions, including both globular and dendritic structures are seen in Fig. 4. Iron is present within α grains; it is light blue colour in bright field, with round or square shapes. Its presence was confirmed by EPMA.

The equi-axed structure suggests that it could have been either annealed or slowly cooled. The fact of a high microhardness value and absence of twins throughout the section precludes the possibility of cold working followed by annealing. Therefore, the object was cast with a slow cooling rate.

**Composition:**

**AAS:** too corroded for analysis.

**Microanalysis:**

The composition of the best-preserved area (1200x) of the polished section was measured using SEM/EDS, and its semi-quantitative result is listed below. It is a binary alloy of Cu-Sn.

| Cu | Sn | Fe | S | Si | Total |
|---|---|---|---|---|---|
| 82.8 | 12.9 | 1.3 | 0.7 | 0.3 | 98.0 |

**Microhardness:** 154 Hv

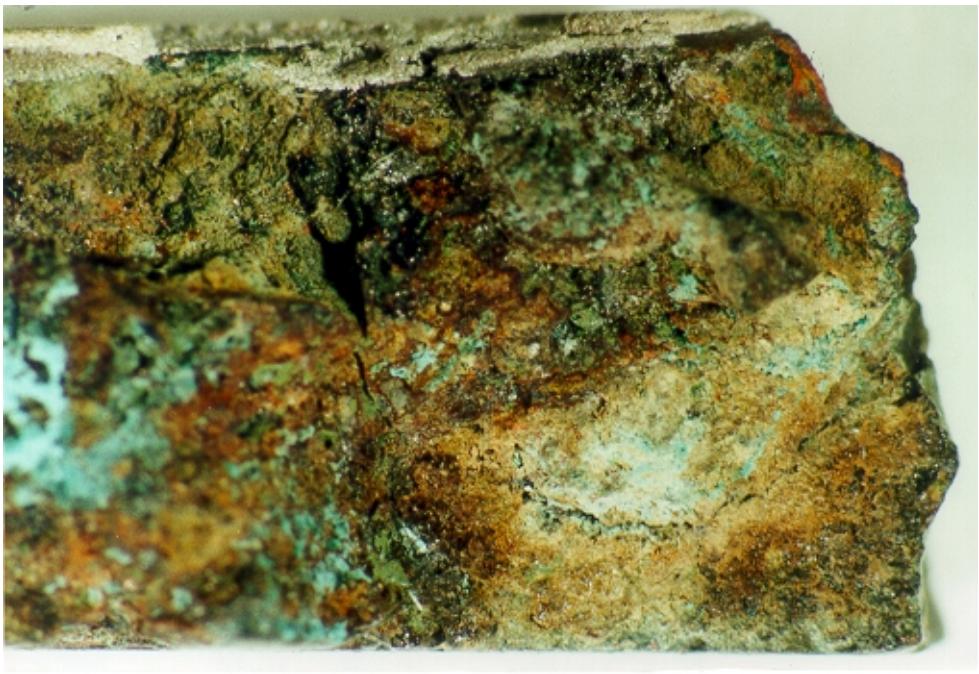


Fig. 1 One surface of the fragment. Width of the image = 5.2 mm.

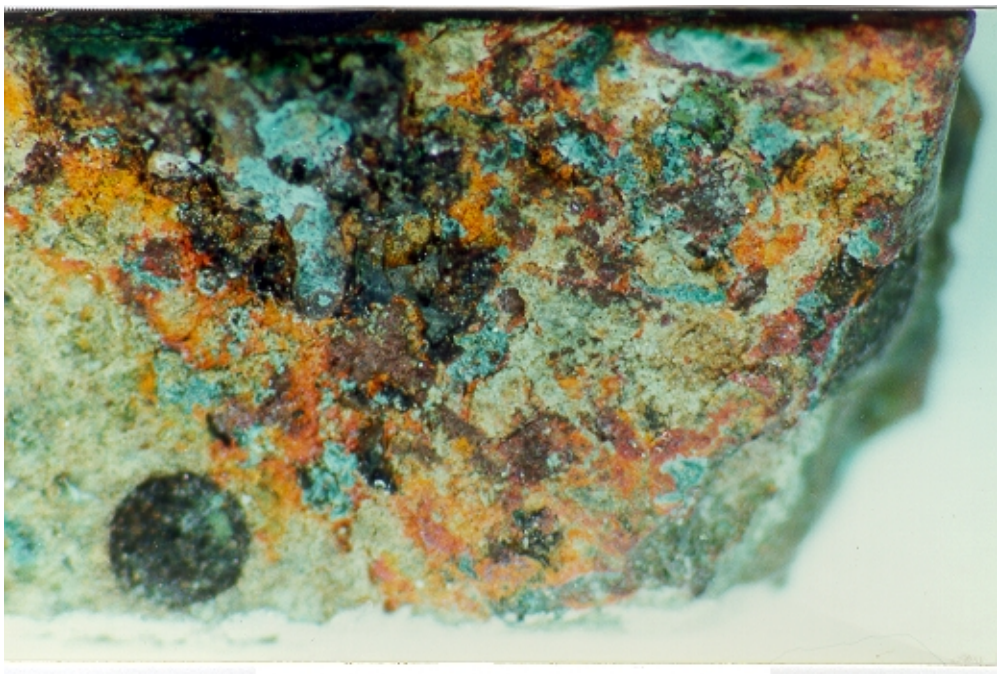


Fig. 2 The other surface of the fragment. Width of the image = 5.2 mm.

Fig. 3 Metallographic section. Length of the section = 11.5 mm.

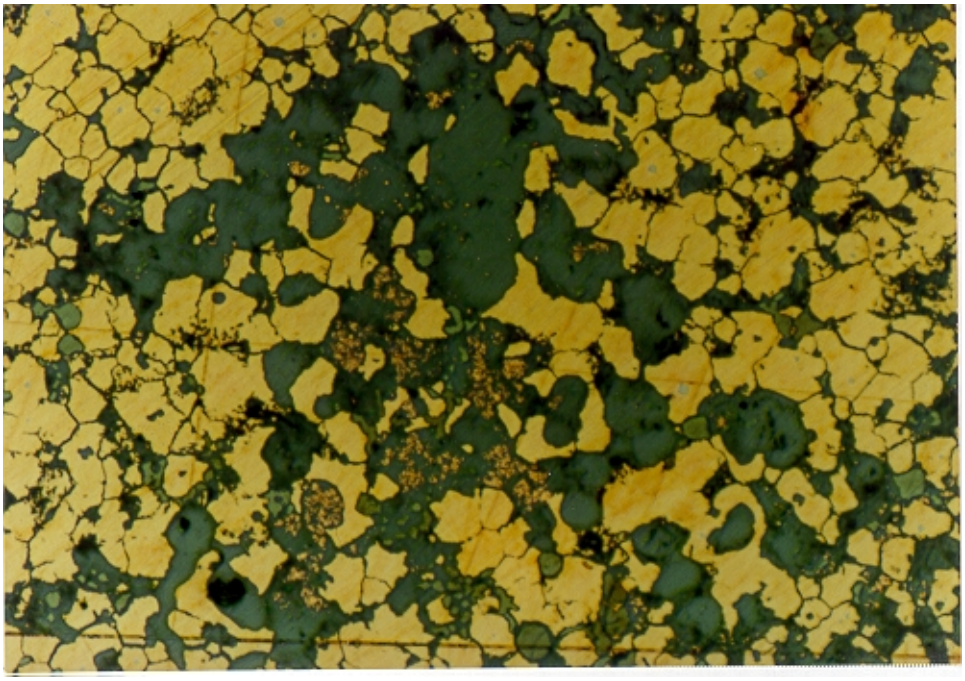


Fig. 4 Photomicrograph of corroded metal in the middle of the specimen, showing redeposited Cu within cuprite. The small light blue dots within the grains are iron inclusions.
BF. Width of the image = 0.4 mm.

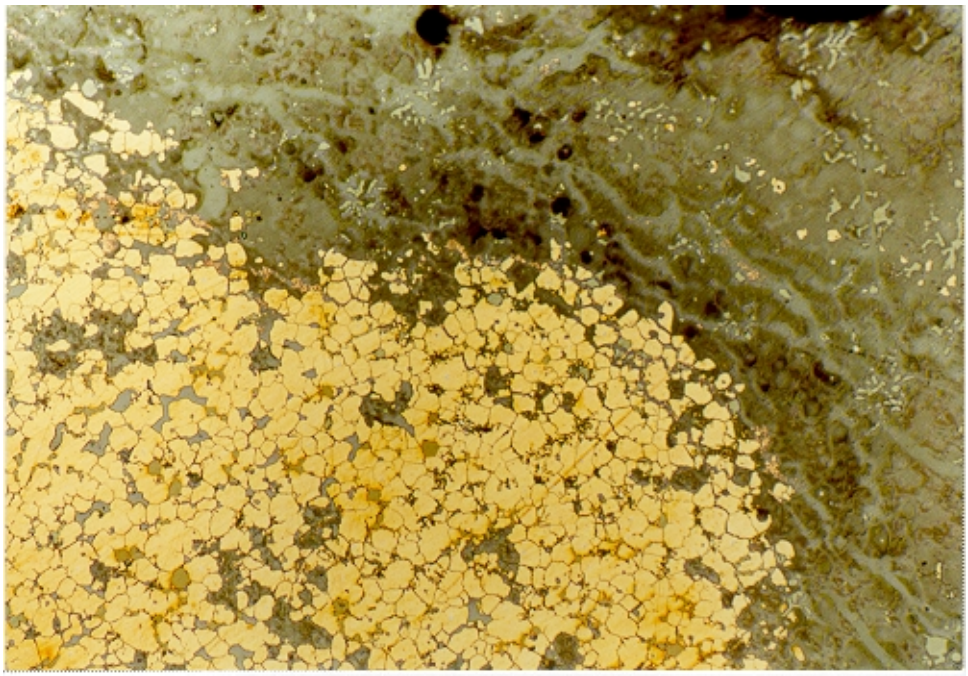


Fig. 5 Photomicrograph of corroded surface, showing corrosion development from surface into metal. BF. Width of the image = 0.9 mm.

## CORROSION

### XRD results:

Surface sample: malachite, azurite, cassiterite, cuprite, brochantite.

### Metallographic observation:

Fig. 3 shows that corrosion overburden is present on both surfaces, the thickest part is 0.15 mm. One of the original surfaces is preserved well, while the other one is disrupted by corrosion. Corrosion goes deep to the metal core following the grain boundaries (Fig. 5). Small areas of redeposited Cu are seen within cuprite inside the metal (Fig. 4) and in the totally corroded area (Fig. 5). Stripes of redeposited Cu are seen in cracks as well. It seems that Cu in this case redeposited within cuprite. A big pit of corrosion is seen inside the metal (Fig. 7), which will be discussed below.

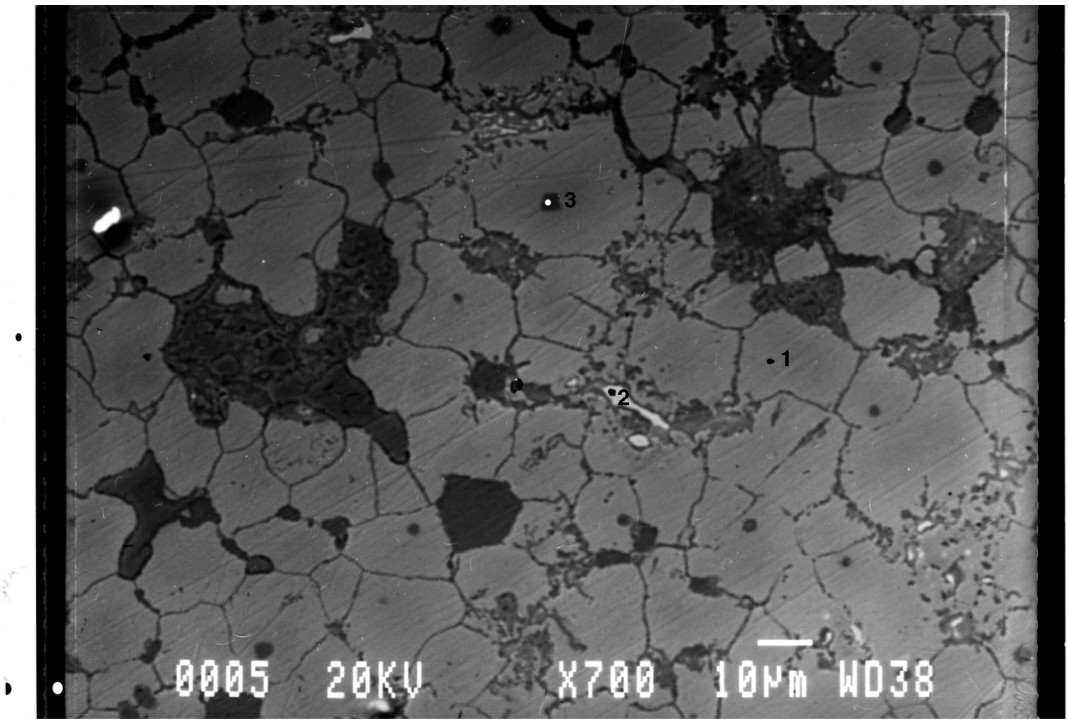



Fig. 6 BEI of corroded metal. Point 1, 2, 3 are α, δ and Fe inclusion, respectively.
Grain size estimated from this image is 0.015mm.

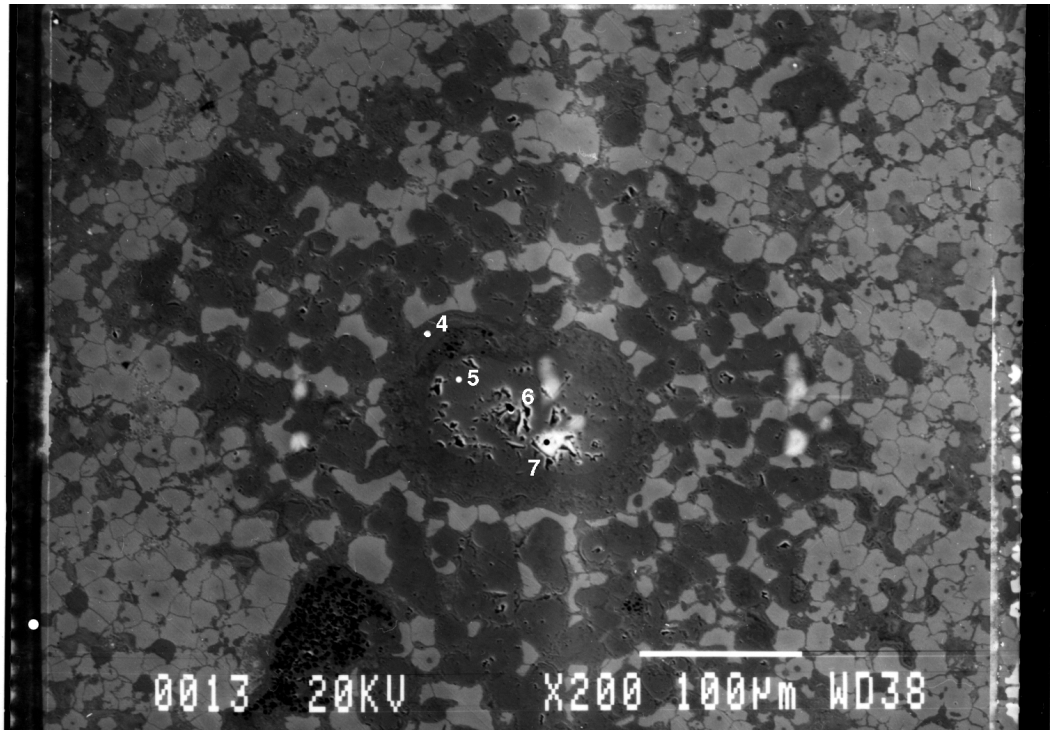



Fig. 7 BEI of corroded Pb globule, showing original inclusion of Pb in copper.

**Microanalysis:**

Elemental linescan using EPMA was carried out across the metal; the plot of composition is shown in Fig. 8. The areas with low totals correspond to intergranular corrosion. The contents of Pb and that of Fe are higher in corroded boundaries than that in intact metallic phases, although iron inclusions contain more Fe (see point 3 of EPMA data).

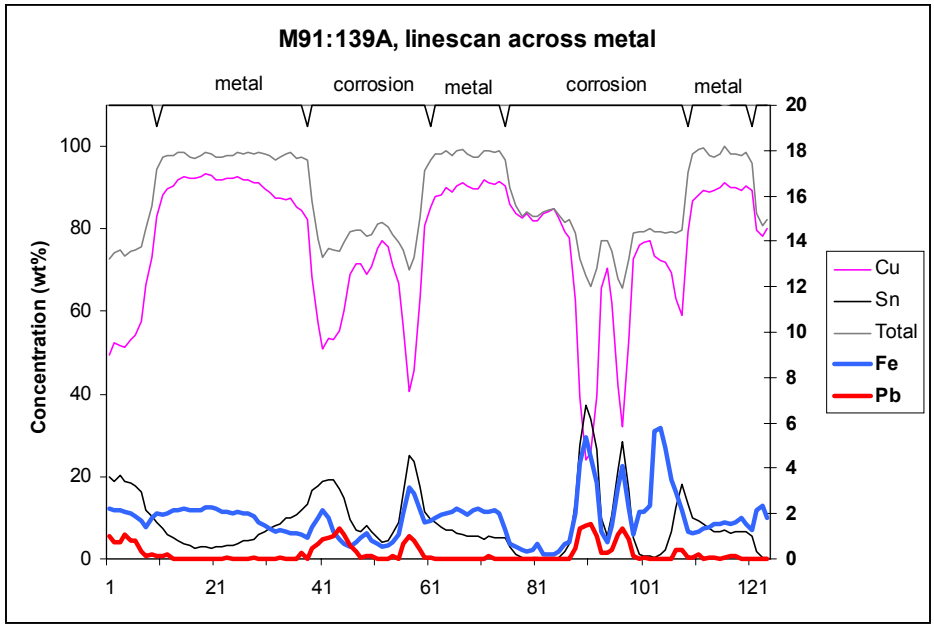



Fig. 8 EPMA linescan across metal, showing intergranular corrosion (the area of low total)

Different phases of the metal and iron inclusions were analysed by SEM/EDS. An investigation of the big pit of corrosion mentioned above has also been carried out using SEM/EDS, which shows it is lead related corrosion behaviour. The composition of this pit from its centre outward is: lead, cuprite, and copper sulphide, their semi-quantitative results along with the results of different phases (Fig. 6) are listed below. The low totals are probably due to porosity resulted from corrosion.

| Point | Cu | Sn | Fe | Cl | S | Total | Description |
|---|---|---|---|---|---|---|---|
| **1** | 79.9 | 11.4 | 0.8 | | | 92.1 | α |
| **2** | 60.5 | 31.2 | | | | 91.7 | δ |
| **3** | 10.7 | | 79.3 | | | 90.0 | Fe inclusion in α phase |
| **4** | 67.3 | | 0.2 | | 19.7 | 87.2 | Copper sulphide |
| **5** | 65.7 | | 0.1 | 0.2 | | 66.0 | Cuprite |
| **6** | 66.0 | | | 0.1 | | 66.1 | Cuprite |
| **7** | | | | | | | Qualitatively determined as lead |

This area of corrosion was probably the result of replacement of lead. This is confirmed by the remains of lead in the centre. The original lead inclusion was corroded then replaced in part by cuprite and copper sulphide.
Microanalysis on the black corrosion on the surface shows it is rich in Fe. Microanalysis shows that the yellowish corrosion product is comprised of 55% Cu, 32% Sn, and 10% Fe. Fe in corrosion could result from accumulation from soil or other sources such as pigments for paintings.

**SUMMARY**

It is a binary alloy of Cu-Sn. The best estimate of bulk composition determined by SEM/EDS is 83% Cu, 13% Sn and 1.3% Fe. Its equi-axed structure indicates a slow cooling rate. Inclusions of S and Fe are present. It is deeply corroded. Corrosion developed from surface into metal along grain boundaries. Redeposited Cu is present within cuprite on surfaces and inside the metal.

## GENERAL

**Object Number:** M91:139B
**Excavation Date:** 1994
**Origin:** Tianma-Qucun site

**Object:** Vessel/*ding*
**Date:** Late Western Zhou
**Fragment Weight:** 15.4 g
**Fragment size:** 36 mm long, 7.7–12.3 mm in diameter

**General description:**

It is a rod assigned the same object Number M91:139 as the previous object by archaeologists. Its overall view is shown in Fig. 1. It seems like an individual object rather than a fragment of an object. Corrosion index is 4. The green powdery corrosion product is suspected to be bronze disease (Fig. 2). X-ray radiography shows there is a crack in this area.


Fig. 1 Overall view of the rod.

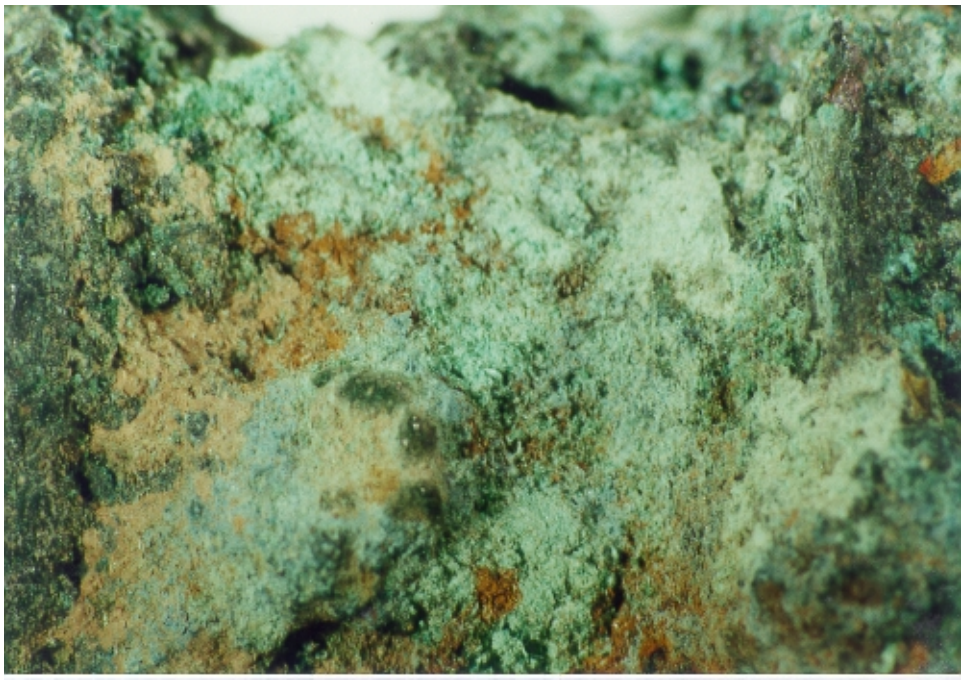


Fig. 2 Bronze disease on the surface, confirmed as atacamite and paratacamite by XRD.
Width of the image = 0.6 mm.

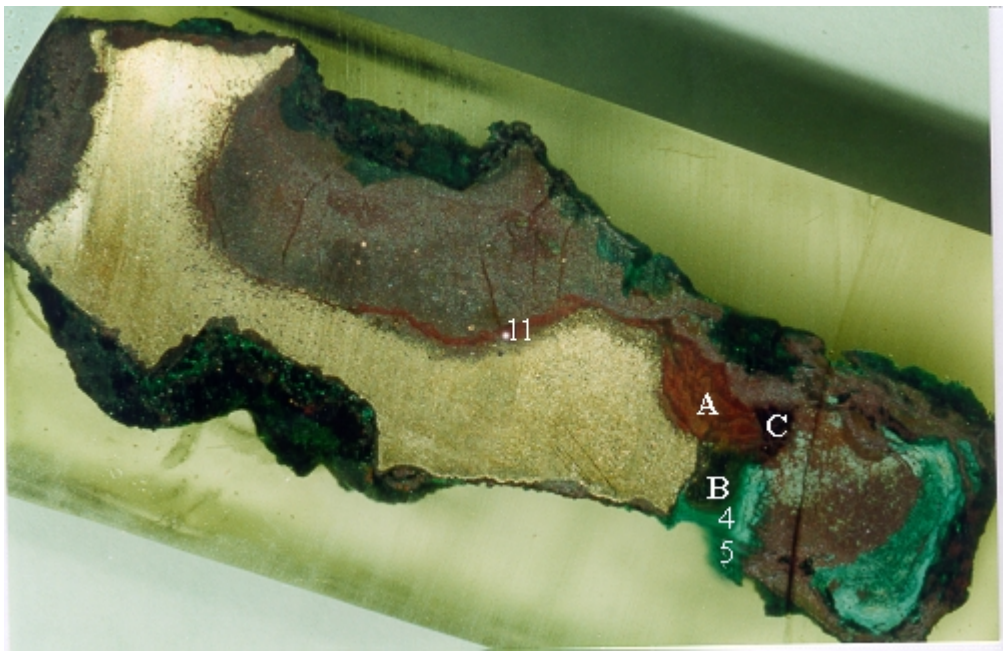



Fig. 3 Metallographic section along the long axis, showing analysed areas abd EPMA points.
Length of the section = 36 mm.

## TECHNICAL STUDIES OF METAL

### Metallographic structure:

The rod was mounted in epoxy and then sectioned along the long axis through the bronze disease area (Fig. 3). The estimated original dimension measured in the metallographic section is 7.7-12.3 mm in diameter. It has a cast dendritic structure (Fig. 4). The estimated dendritic arm spacing is 0.02 mm. The presence of casting pores (Fig. 4) implies that the gas permeability of the mould from which the object was made was not good.

### Composition:

**AAS**: too corroded for analysing

**Microanalysis:**

SEM/EDS Semi-quantitative analysis was carried out on the least corroded area (800x), the best estimate of bulk composition is as follow. Lead is present as small globules and confirmed by point analysis (Fig. 4). The low total could be due to the porosity and corrosion.

| Cu | Sn | Pb | Total |
|---|---|---|---|
| 70.0 | 12.1 | 1.6 | 83.7 |

**Microhardness:** 122Hv

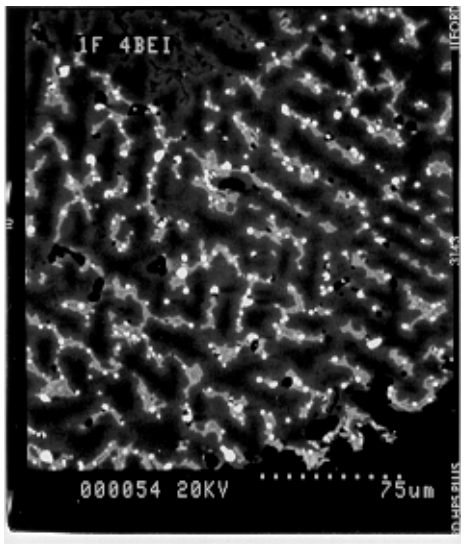



Fig. 4 BEI of dendritic microstructure.
Dendritic arm spacing is 0.021mm.

## CORROSION

### XRD results:

Light green powdery corrosion products suspected to be bronze disease: atacamite, paratacamite, nantokite and cassiterite.

### Metallographic observation:

The object is corroded badly, but the original surface is still roughly apparent. The small end with bronze disease is totally corroded. In some areas (Fig. 3) 4/5 of the original metal (i.e. the width of the cross section) is totally corroded without any remnant metallic phases. In most areas of the polished section, α phases remain, but δ phases are removed. δ phases are only seen in a small corroded area on a surface.

The light green corrosion at the small end is proved to be bronze disease by XRD. Its photomicrograph is shown in Fig. 5. The zone of reddish band against metal (area A) looks like a mixture of nantokite and cuprite (see Fig. 6). The transition area (area B) between bronze disease and nantokite is shown in Fig. 7 (corresponding to Fig. 8), its composition analysed by EPMA is listed below. Crystals are evident in backscattered electron image at area C (Fig. 9), they appear red to black in cross polars (Fig. 10). The cubic structure of these crystals indicates that they are cuprite, their low concentration of Cu (76.9% Cu in point 7) is probably due to the feature of the crystals, which are not flat in the orientation where the analyses were conducted. Redeposited Cu is seen in the corrosion zone of cuprite, and in the cracks as well (Fig. 11). A dendrite copper grain shown in Fig. 12 could be the result of destannification, since δ phases were removed in this area.

### Microanalysis:

EPMA was carried out on this sample; the points analyzed were marked in Fig. 3, 8 and 9. Pseudomorphic dendritic structure is still seen in the corroded area. The presence of Cl in the corroded metal indicates that bronze disease has penetrated into the metal. Compared with Pb globules in the uncorroded metal (Fig. 4), Pb grains in the corroded part (Fig. 9) are much bigger and different in shape, which are corrosion product, probably $PbSO_4$ according to the ratio of Pb/S and the total.

| Point | Description |
|---|---|
| **1** | Lead corrosion product |
| **2** | Corroded α, seems to have been converted to nantokite |
| **3** | Corroded δ |
| **4** | Copper chloride |
| **5** | Copper chloride |
| **6** | Cuprite crystal |
| **7** | Cuprite crystal |
| **8** | Nantokite |
| **9** | Porous copper chloride |
| **10** | Mixture of Cu(I) and Cu(II) chloride |
| **11** | Probably mixture of nantokite and cuprite based on its red colour and Cl content |

| Point | Cu | Fe | Pb | As | S | Cl | Ag | Sb | Bi | Hg | Cd | Sn | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 0.89 | 0.04 | 65.66 | 0.00 | 9.84 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.10 | 0.02 | 76.55 |
| **2** | 47.27 | 0.01 | 1.10 | 0.00 | 0.12 | 22.96 | 0.02 | 0.00 | 0.05 | 0.00 | 0.00 | 10.45 | 82.14 |
| **3** | 17.31 | 0.05 | 4.34 | 0.08 | 0.37 | 5.33 | 0.13 | 0.00 | 0.46 | 0.00 | 0.00 | 47.02 | 75.26 |
| **4** | 53.31 | 0.00 | 0.01 | 0.52 | 0.05 | 16.31 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.02 | 70.75 |
| **5** | 52.16 | 0.00 | 0.08 | 0.87 | 0.11 | 13.74 | 0.01 | 0.00 | 0.05 | 0.09 | 0.00 | 0.14 | 67.79 |
| **6** | 75.28 | 0.00 | 0.00 | 0.15 | 0.01 | 0.00 | 0.00 | 0.02 | 0.01 | 0.00 | 0.00 | 0.03 | 75.76 |
| **7** | 76.89 | 0.00 | 0.00 | 0.39 | 0.03 | 1.17 | 0.01 | 0.00 | 0.00 | 0.01 | 0.01 | 0.13 | 78.95 |
| **8** | 61.49 | 0.01 | 0.05 | 0.00 | 0.01 | 35.51 | 0.03 | 0.00 | 0.00 | 0.06 | 0.02 | 0.12 | 97.47 |
| **9** | 38.05 | 0.00 | 0.06 | 0.00 | 0.08 | 16.40 | 0.00 | 0.00 | 0.00 | 0.06 | 0.00 | 0.10 | 55.02 |
| **10** | 37.53 | 0.11 | 0.77 | 0.00 | 0.19 | 25.44 | 0.14 | 0.01 | 0.00 | 0.05 | 0.02 | 0.06 | 64.77 |
| **11** | 43.10 | 0.01 | 0.16 | 0.09 | 0.00 | 32.94 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 76.47 |

## SUMMARY

It is a binary alloy of Cu-Sn with a cast dendritic structure. The best estimate of bulk composition determined by SEM/EDS is 70% Cu, 12% Sn and 1.6% Pb. Lead is present as small globules in eutectoids. This is the worst sample of bronze disease in this project. Nantokite is also present based on EPMA and XRD results. Almost all δ phases had corroded with α phases being preserved. Redeposited Cu is present within cuprite on surfaces and in cracks. It is likely that destannification occurred on this sample.

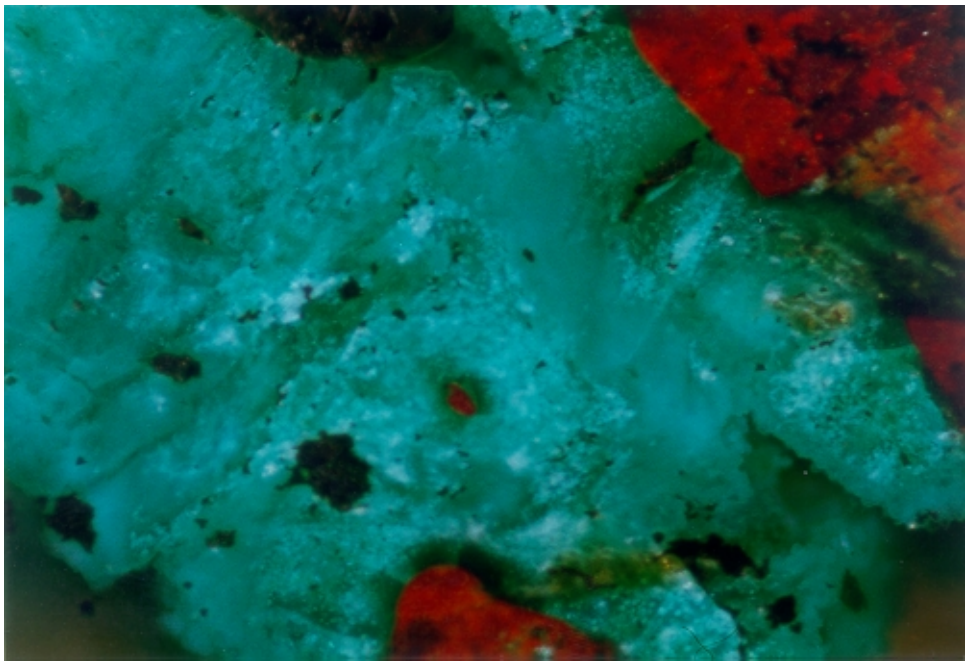


Fig. 5 Photomicrograph of bronze disease (green part).
C/P. Width of the image = 2 mm.

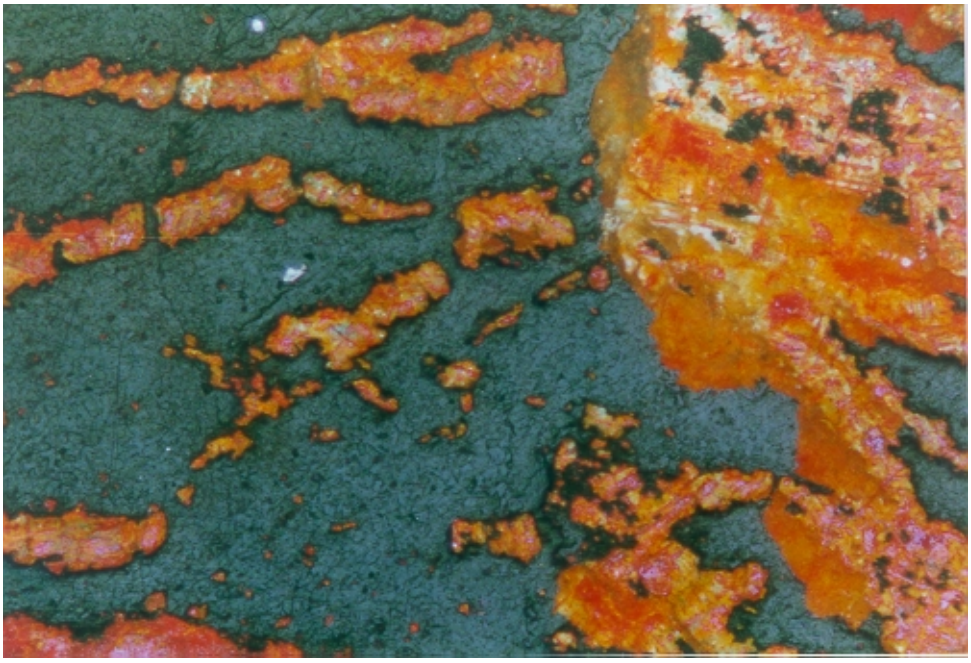


Fig. 6 Photomicrograph of nantokite (dark grey part) with cuprite (area A in Fig. 3).
C/P. Width of the image = 2 mm.

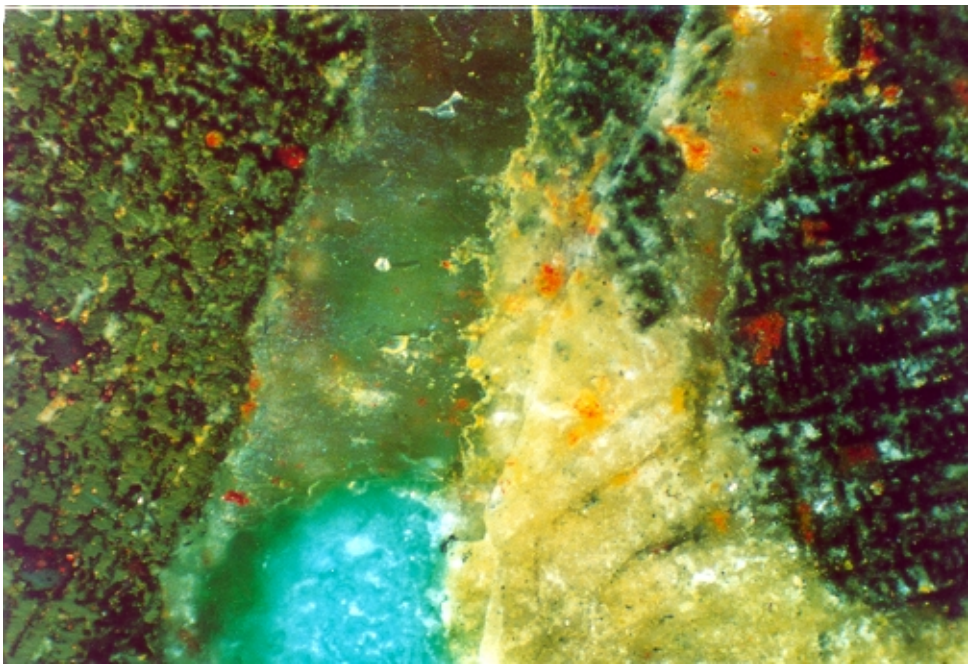


Fig. 7 Photomicrograph of bronze disease and nantokite (Area B in Fig. 3).
C/P. Width of the image = 1 mm.

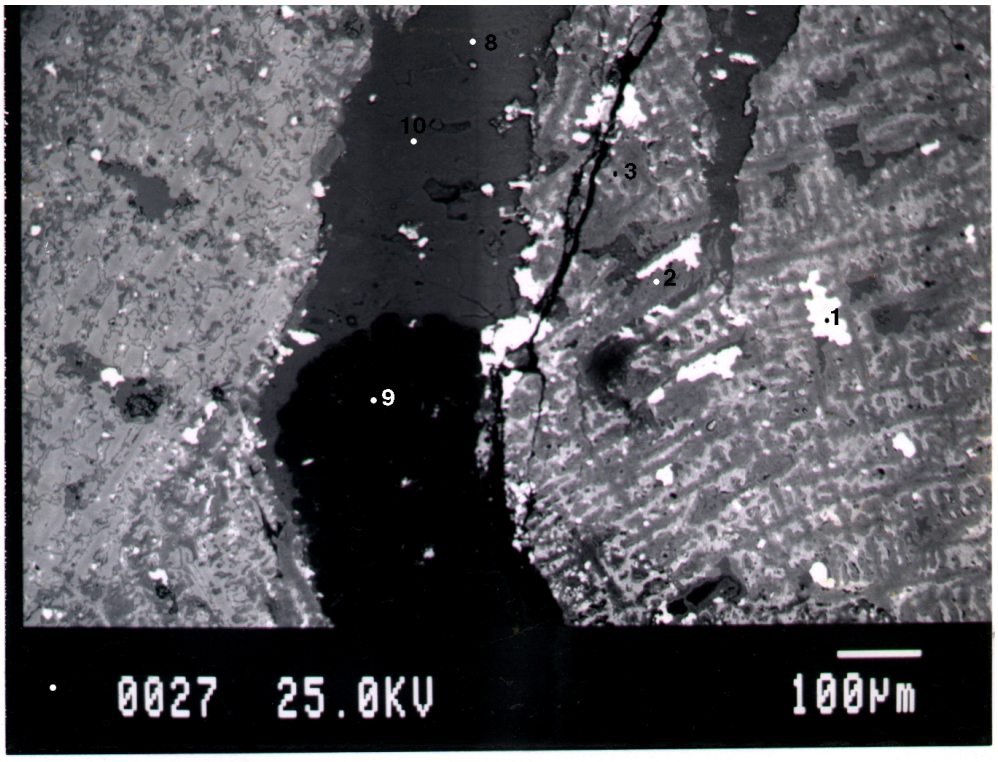



Fig. 8 BEI of the same area as Fig. 7, showing EPMA points.

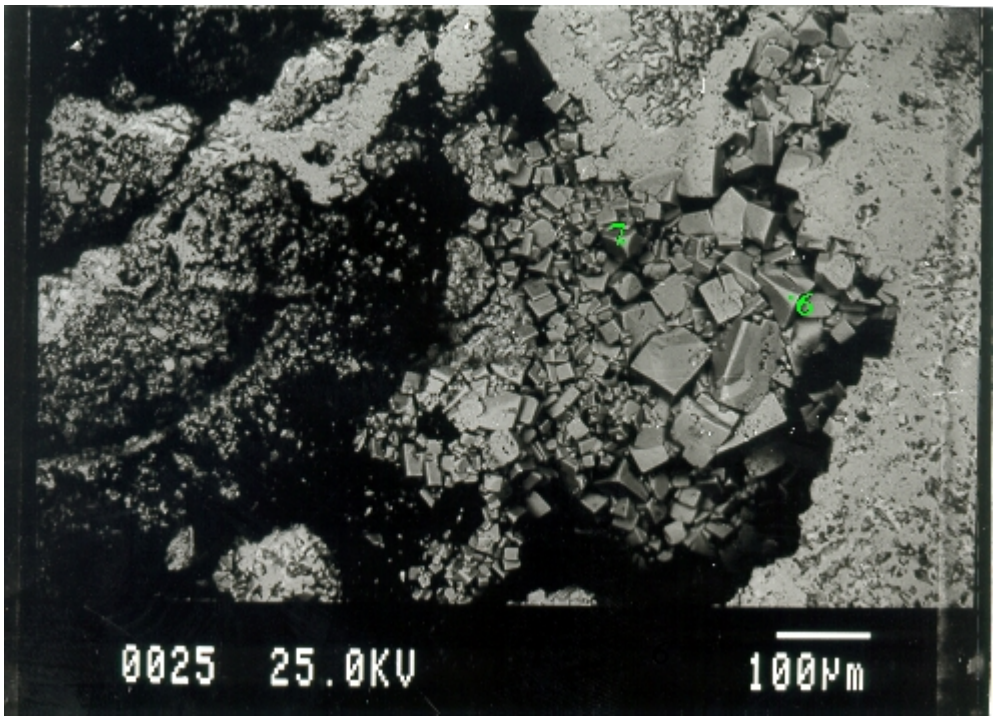



Fig. 9 BEI of cuprite crystals in a crevice, showing EPMA points.

Fig. 10 Photomicrograph of cuprite crystals corresponding to Fig. 9 (Area C in Fig. 3). C/P. Width of the image = 1 mm.

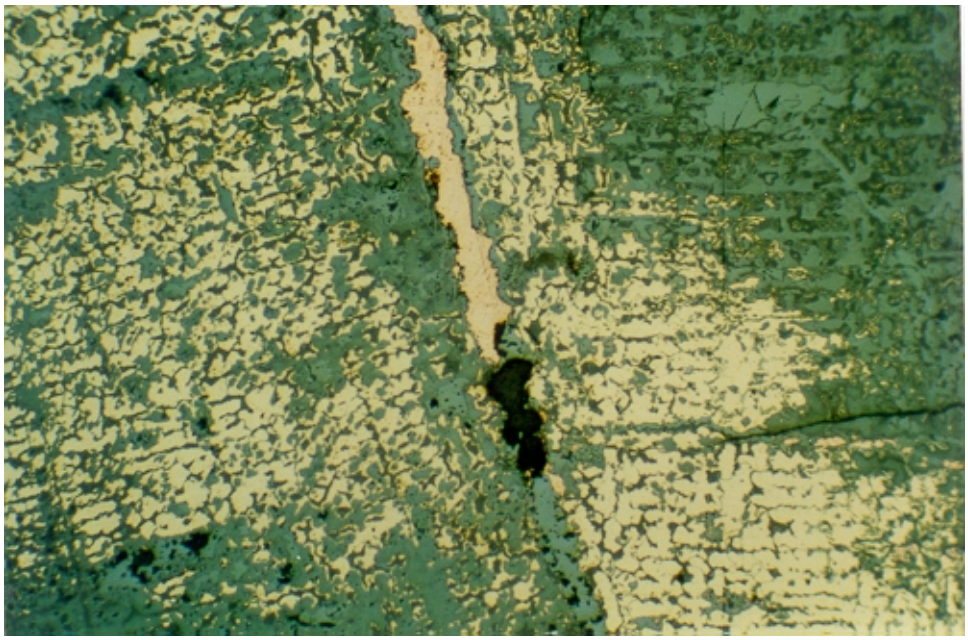


Fig. 11 Photomicrograph of redeposited Cu in a crack, confirmed by SEM/EDS.

BF. Width of the image = 1 mm.

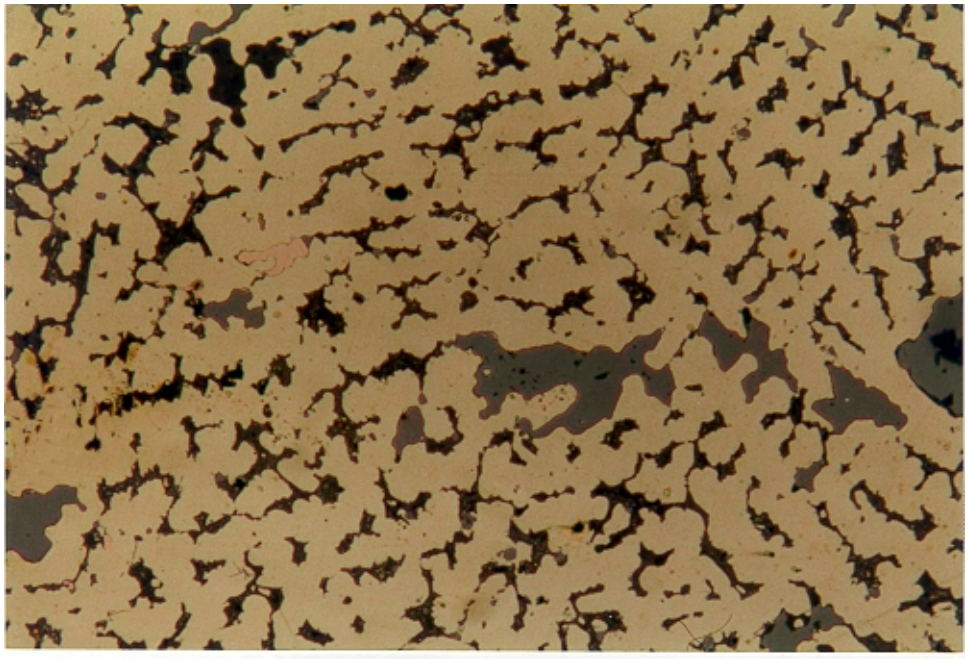


Fig. 12 Photomicrograph of redeposited Cu in shape of corroded eutectoid.

BF. Width of the image = 0.5 mm.

## GENERAL

**object Number:** M91:140
**Excavation Date:** 1994
**Origin:** Tianma-Qucun site

**Object:** vessel/*ding*
**Date:** Late Western Zhou
**Fragment Weight:** 16.2 g
**Fragment size:** 38x20x2.8 mm

**General description:**

This flat fragment has all edges broken. Corrosion index is 3. There is a corrosion overburden on the surface, including green, yellow and black corrosion products. The powdery green corrosion product on the left upper corner in Fig. 1 is suspected to be bronze disease. The fibrous black material looks like charcoal (Fig. 1). No decoration is apparent. It is probably from the sidewall or base of the object.

## TECHNICAL STUDIES OF METAL

**Metallographic structure:**

A section cut through the full width of the fragment was taken for metallographic observation. The estimated original thickness is 2.8 mm as measured in the metallographic section. After etching, it shows an equi-axed structure, with sulphide inclusions. Equi-axed grain structure is evident in the corroded part (Fig. 2). The estimated grain size is 0.019 mm. It must have been cooled slowly.

**Composition:**

**AAS:**

| **Cu** | **Sn** | **Pb** | **Fe** | **As** | **Co** | **Zn** | **Ni** | **Ag** | **Au** | **Sb** | **Bi** | **total** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ( | wt% | | ) | ( | | | ppm | | | | ) | (wt%) |
| 79.85 | 12.02 | 0.55 | 1.12 | nd | nd | 459 | 204 | 510 | nd | nd | nd | 93.65 |

**Microanalysis:**

See corrosion section.

**Microhardness:** 110Hv

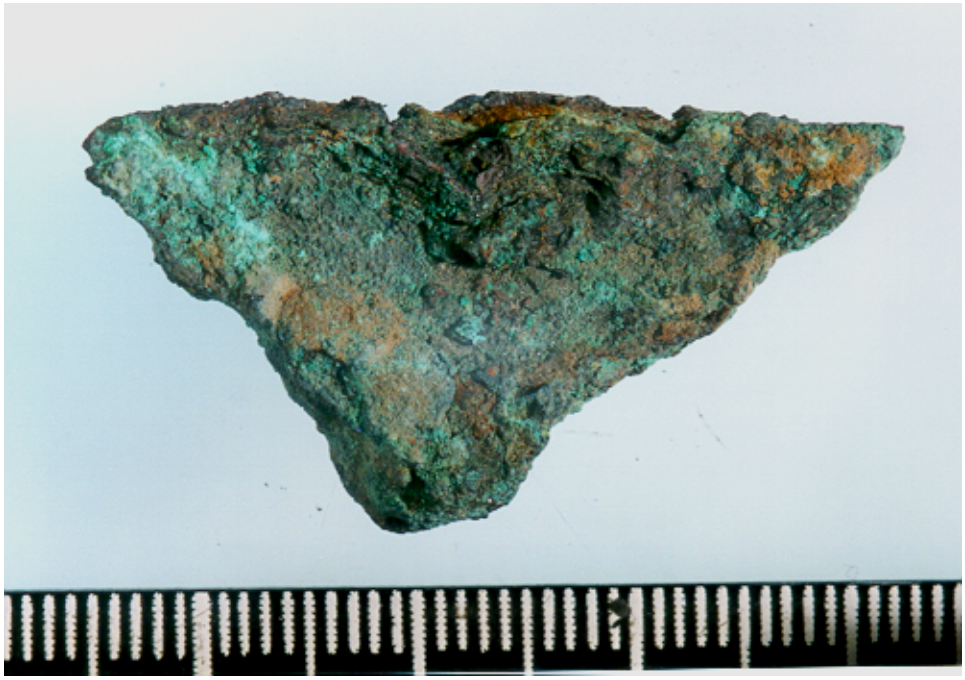


Fig. 1 General view of the fragment. Bronze disease is suspected at left upper corner.

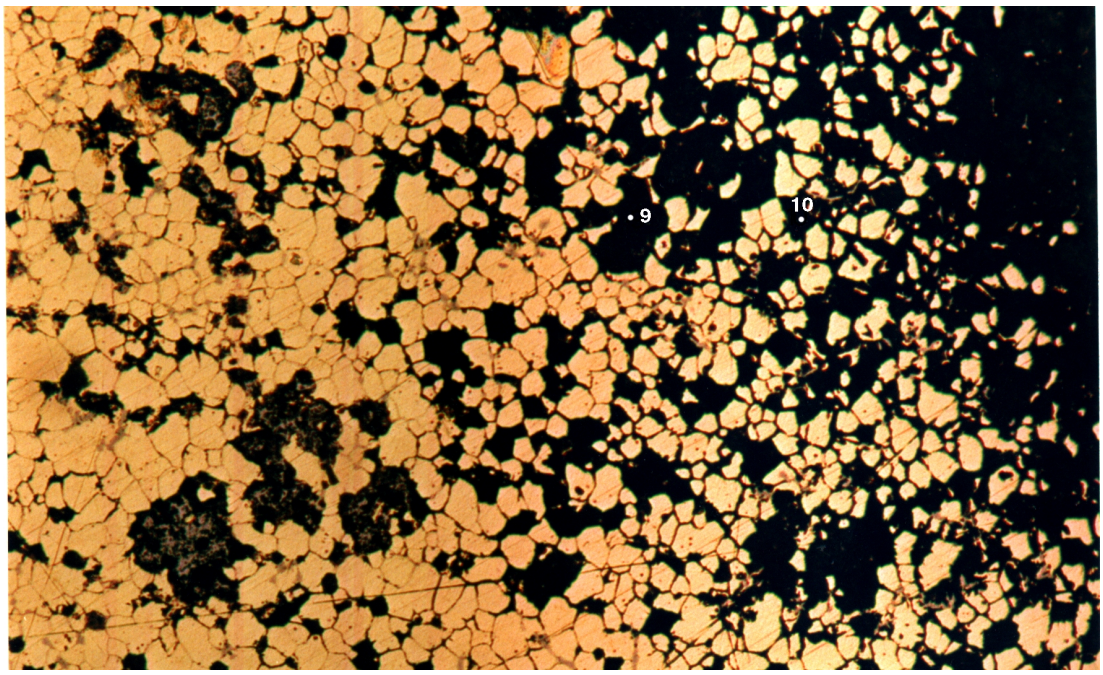



Fig. 2 Photomicrograph of the heavily corroded corner attacked by chloride, confirmed by EPMA (points 9 & 10). BF. Width of the image = 1mm.

## CORROSION

**XRD results:**

Green powdery material on the surface: atacamite, cuprite.

Black corrosion products: quartz, cuprite, with goethite, hematite, and azurite.

**Metallographic observation:**

The original surfaces are evident in most areas but disrupted in some. Corrosion follows the grain boundaries. A corner is badly corroded, with most metallic phases gone (Fig. 2). The corroded areas are almost black in bright field and appear dark grey in cross polarised light. At this corner, there are layers of corrosion, which are light blue, brown, red, and mixture of red and black in sequence from metal outward (Fig. 3). Redeposited Cu is seen in cuprite present both inside the metal (Fig. 4) and on the surface (Fig. 5). Redeposited Cu is also present in corrosion voids in the metal, it must have been deposited from copper chloride. Slip lines in the corroded area or on the surface is likely the result of crystallographic corrosion, because twin lines are not observed in the etching sample.

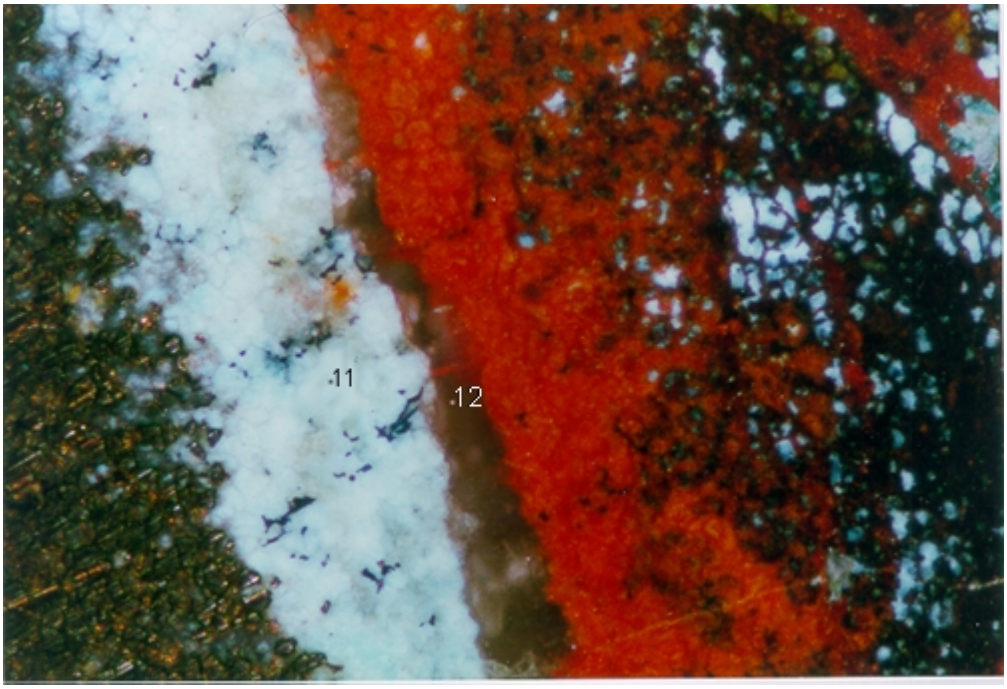



Fig. 3 Photomicrograph of disrupted original surface by chloride.

BF. Width of the image = 1mm.

**Microanalysis:**

EPMA point analyses were carried out on a corrosion void in the metal (Fig. 6). It contains Cu, Cl , Pb and Sn. It is a casting void or a corrosion pit resulted from attack of $Cl^-$. Iron inclusions are seen in α grains (point 7).

EPMA point analyses were also carried out on this badly corroded area (Figs. 2 & 3) and redeposited Cu in Fig. 4. The results are shown below:

| Point | Description |
|---|---|
| **1, 3, 6** | Matrix of the a corrosion void |
| **2** | Corrosion in the void |
| **4** | α |
| **7** | Fe inclusion |
| **8** | Redeposited Cu |
| **9, 10** | Corroded area at a corner |
| **11** | The innermost layer of corrosion |
| **12** | A layer between the innermost layer and cuprite layer |

| Point | Cu | Fe | Au | Ni | Sn | Pb | Zn | Ag | Hg | As | Sb | Bi | Co | S | Cl | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 77.74 | 0.17 | 0.03 | 0.01 | 1.16 | 0.88 | 0.00 | 0.12 | 0.00 | 0.24 | 0.00 | 0.09 | 0.00 | 0.18 | 3.14 | 83.75 |
| **2** | 17.45 | 0.20 | 0.00 | 0.00 | 10.44 | 54.82 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 10.32 | 1.95 | 95.24 |
| **3** | 51.18 | 0.32 | 0.03 | 0.00 | 2.16 | 6.85 | 0.00 | 0.03 | 0.00 | 0.06 | 0.00 | 0.08 | 0.00 | 0.79 | 20.87 | 82.37 |
| **4** | 85.94 | 1.23 | 0.00 | 0.00 | 9.86 | 0.09 | 0.00 | 0.01 | 0.01 | 0.00 | 0.00 | 0.04 | 0.00 | 0.00 | 0.01 | 97.19 |
| **6** | 21.46 | 4.25 | 0.00 | 0.00 | 40.00 | 2.62 | 0.00 | 0.00 | 0.00 | 0.03 | 0.00 | 1.05 | 0.00 | 0.64 | 7.21 | 77.25 |
| **7** | 20.03 | 61.93 | 0.08 | 0.06 | 7.05 | 0.21 | 0.01 | 0.01 | 0.10 | 0.00 | 0.00 | 0.05 | 0.18 | 0.25 | 0.02 | 89.98 |
| **8** | 96.51 | 0.09 | 0.00 | 0.00 | 0.08 | 0.00 | 0.00 | 0.07 | 0.00 | 0.00 | 0.01 | 0.03 | 0.00 | 0.01 | 0.00 | 96.79 |
| **9** | 44.32 | 4.40 | 0.04 | 0.00 | 0.29 | 0.00 | 0.00 | 0.17 | 0.15 | 0.03 | 0.00 | 0.00 | 0.00 | 0.00 | 18.99 | 68.38 |
| **10** | 19.29 | 3.89 | 0.00 | 0.01 | 39.79 | 2.51 | 0.00 | 0.09 | 0.00 | 0.00 | 0.00 | 0.84 | 0.00 | 0.35 | 8.79 | 75.53 |
| **11** | 30.92 | 1.85 | 0.07 | 0.00 | 21.12 | 1.45 | 0.00 | 0.15 | 0.00 | 0.00 | 0.00 | 0.05 | 0.01 | 0.11 | 15.96 | 71.71 |
| **12** | 54.97 | 0.02 | 0.11 | 0.00 | 0.19 | 0.00 | 0.00 | 0.13 | 0.10 | 0.09 | 0.04 | 0.08 | 0.00 | 0.04 | 29.93 | 85.68 |

Based on ratio of Cu/Cl, it is likely that Cl is present as nantokite (in which Cu/Cl is 1.79). The area at this corner contains a mixture of cassiterite, nantokite and cuprite, and Fe is richer than in the uncorroded metal.

## SUMMARY

It is a binary alloy of Cu-Sn with an equi-axed structure. The best estimate of composition determined by AAS is 79.9% Cu and 12.0% Sn. There are sulphide inclusions. It is attacked by chloride, which also penetrated into metal core. Redeposited Cu is present within cuprite and chloride in corrosion pits and in cracks.

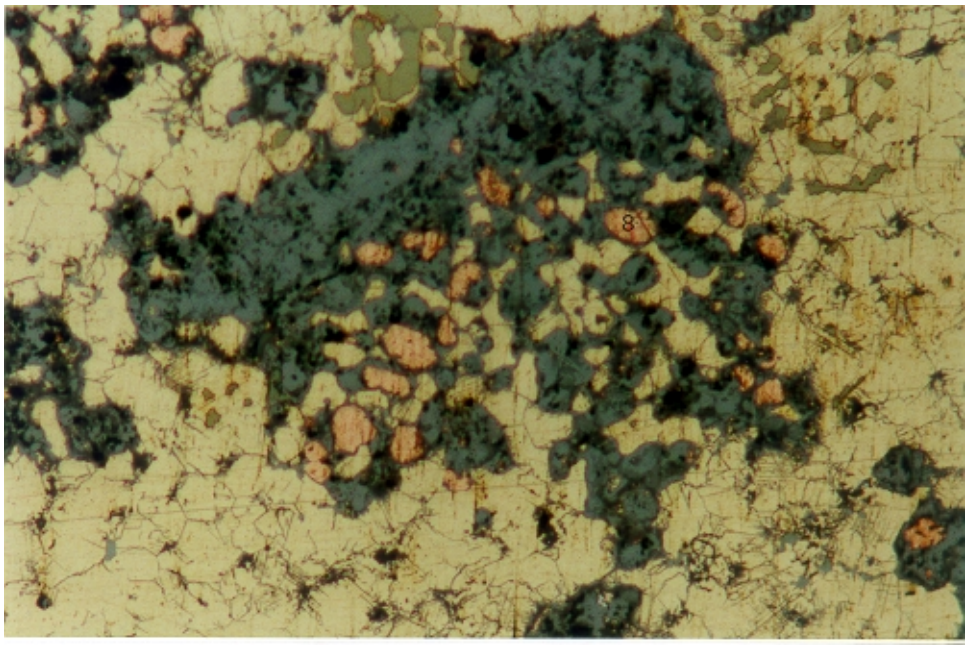



Fig. 4 Photomicrograph of redeposited Cu from cuprite inside the metal, showing EPMA point 8. BF. Width of the image = 0.5 mm.

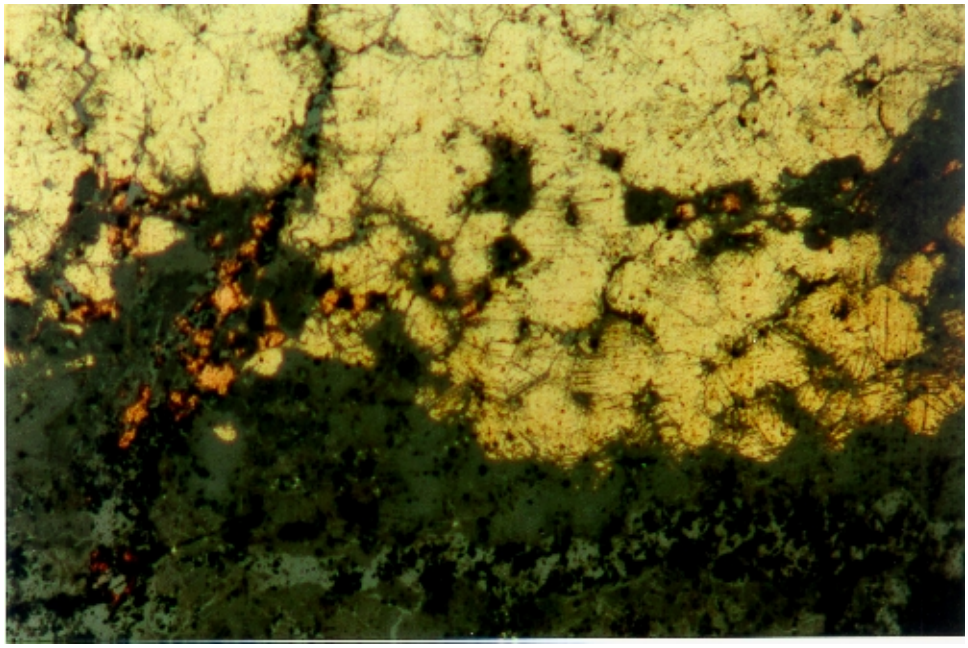


Fig. 5 Photomicrograph of slip lines at an edge and redeposited Cu in a crack. BF. Width of the image = 0.5 mm.

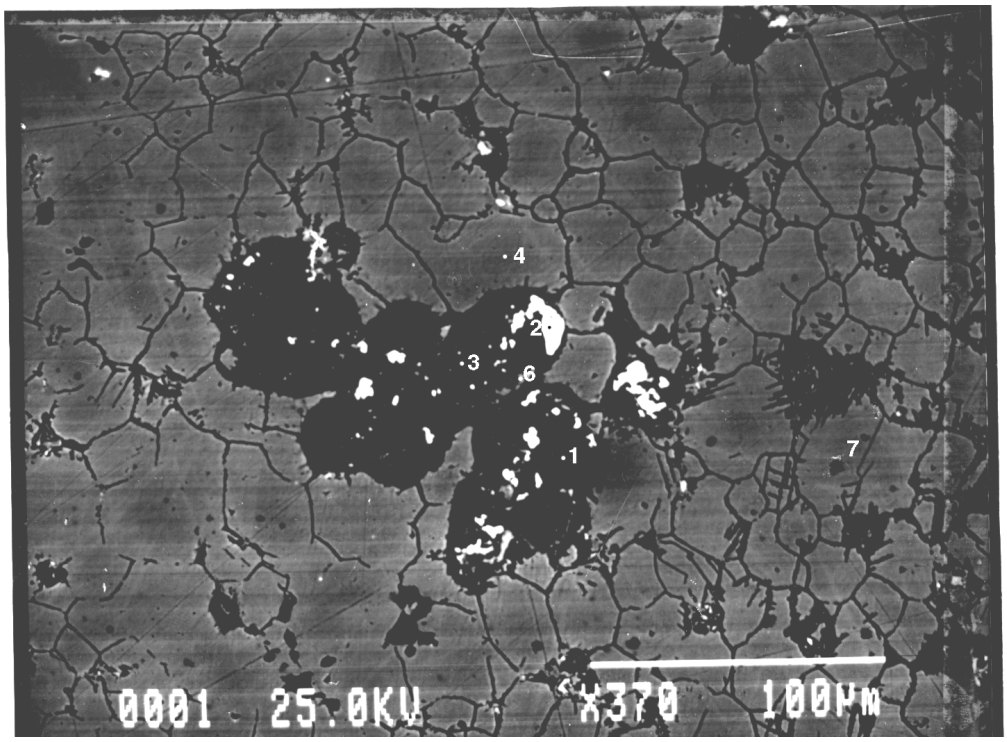



Fig. 6 BEI of a corrosion pit in the metal, showing EPMA points

## GENERAL

**Object Number:** M91:222
**Excavation Date:** 1994
**Origin:** Tianma-Qucun site

**Object:** vessel/round pot
**Date:** Late Western Zhou
**Fragment Weight:** 5.4 g
**Fragment size:** 26x9x1.8 mm

**General description:**

This fragment has all sides broken. Corrosion index is 3. There is a corrosion overburden on the surface, including red, light green and dark green corrosion products. Fibrous malachite can be seen on the surface. Cracks are seen on the surface. No decoration is apparent. This piece is probably from the base or another flat part, since no curve is observed on the cross- sectional surface.

## TECHNICAL STUDIES OF METAL

**Metallographic structure:**

A section cut through the full length of the fragment was taken for metallographic observation (Fig. 1). The estimated original thickness is 1.8 mm as measured in the metallographic section. It has a cast dendritic structure. The average dendritic arm spacing is 0.021 mm. The large (wide) dendrites suggest that this object has probably been cast in a clay mould, as a clay mould would have allowed the molten metal to cool down slowly to form large dendrites (pers. comm. Dr. Northover).

**Composition:**

**AAS:**

| **Cu** | **Sn** | **Pb** | **Fe** | **As** | **Co** | **Zn** | **Ni** | **Ag** | **Au** | **Sb** | **Bi** | **total** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ( | wt% | | ) | ( | | | ppm | | | | ) | (wt%) |
| 55.00 | 12.84 | 0.500 | 0.180 | nd | nd | 1500 | nd | 1000 | nd | nd | nd | 68.77 |

The low total is due to corrosion of this sample.

**Microanalysis:**

SEM/EDS semi-quantitative analysis was carried out on an uncorroded area (390x), the result is as follows, it is a binary alloy of Cu-Sn. Obviously, the SEM/EDS result is the best estimate of bulk composition.

| Cu | Sn | Total |
|---|---|---|
| 81.6 | 17.1 | 98.7 |

**Microhardness:** 152Hv

Fig. 1 Metallographic section. Length of the section = 18 mm.

## CORROSION

### XRD results:

Surface sample: malachite, brochantite, azurite.

### Metallographic observation:

The original surfaces are preserved well, although corrosion has gone all the way through the metal in some parts of the polished section as the cross section in Fig. 1 shows. Inside the core, α phases are preserved but δ phases are partially corroded away. On the surface, two types of corrosion, α-removal corrosion on one side and δ-removal corrosion on the other side, are seen (Figs. 2 & 3).


Fig. 2 Photomicrograph of α-removal corrosion on a surface.

BF. Width of the image = 0.3 mm.

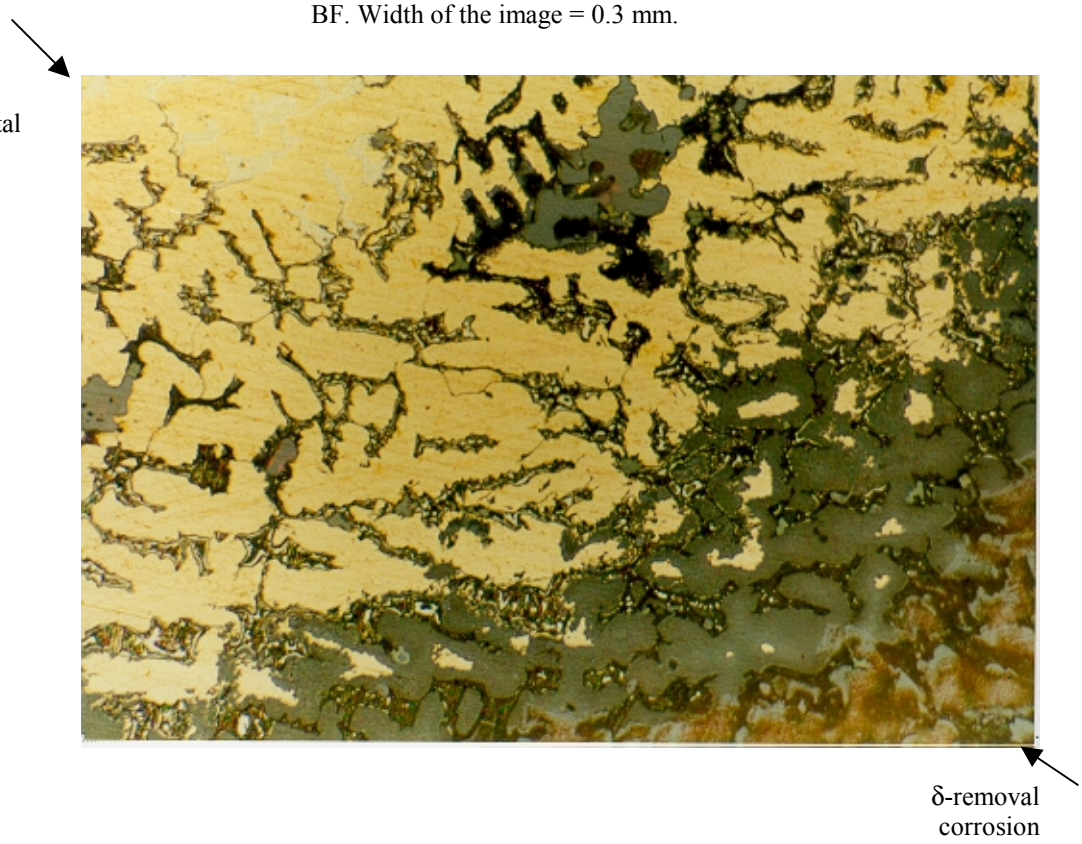



Fig. 3 Photomicrograph of δ-removal corrosion on the other surface.

BF. Width of the image = 0.3 mm.

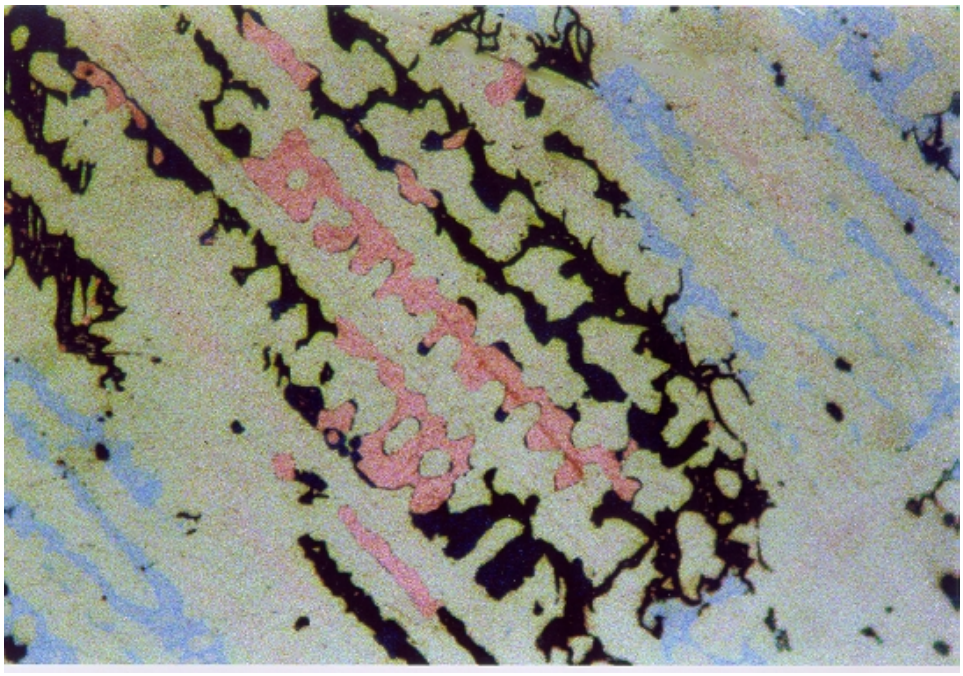


Fig. 4 Photomicrograph of destannification. Etched in aqueous $FeCl_3$.
BF. Width of the image = 0.2mm.

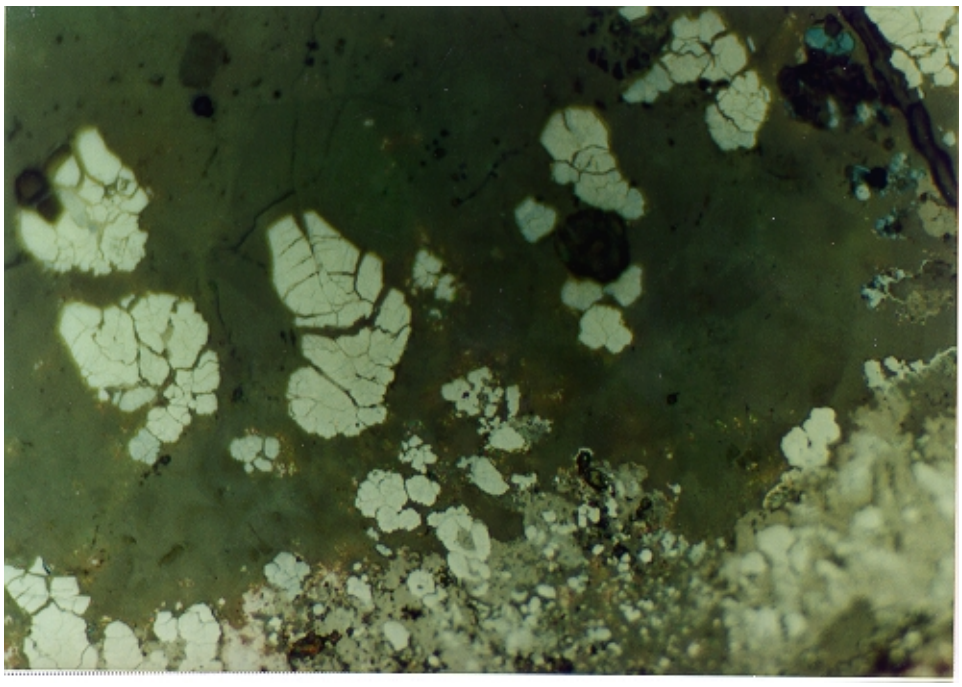


Fig. 5 Photomicrograph of copper sulphide crystals in outmost corrosion layer.
BF. Width of the image = 0.3 mm.

Destannification has occurred on the sample. Cu in Fig. 4 is interpreted as the result of destannification, because it is in the position of the eutectoid, and δ phases in its surrounding area have gone.

Corrosion overburden can be seen on both original surfaces. On the upper surface in Fig. 1, corrosion products are layered structures, they are complex mixtures of cuprite and cassiterite; cuprite; mixture of cuprite, cassiterite and copper sulphide; and copper carbonates in sequence from the metal outwards. These mineral identifications are based on EPMA data, XRD and characteristic colours in the metallographic section. On the other surface, corrosion products are interlaced structures, their inner layers are similar to the upper surface, while their outer layers are more complicated, comprising of malachite (probably brochantite as well), azurite, and copper sulphide. Copper sulphide crystals with fractures are seen in the outermost corrosion layer (Fig. 5). Fibrous malachite is seen in the corrosion (Fig. 6).

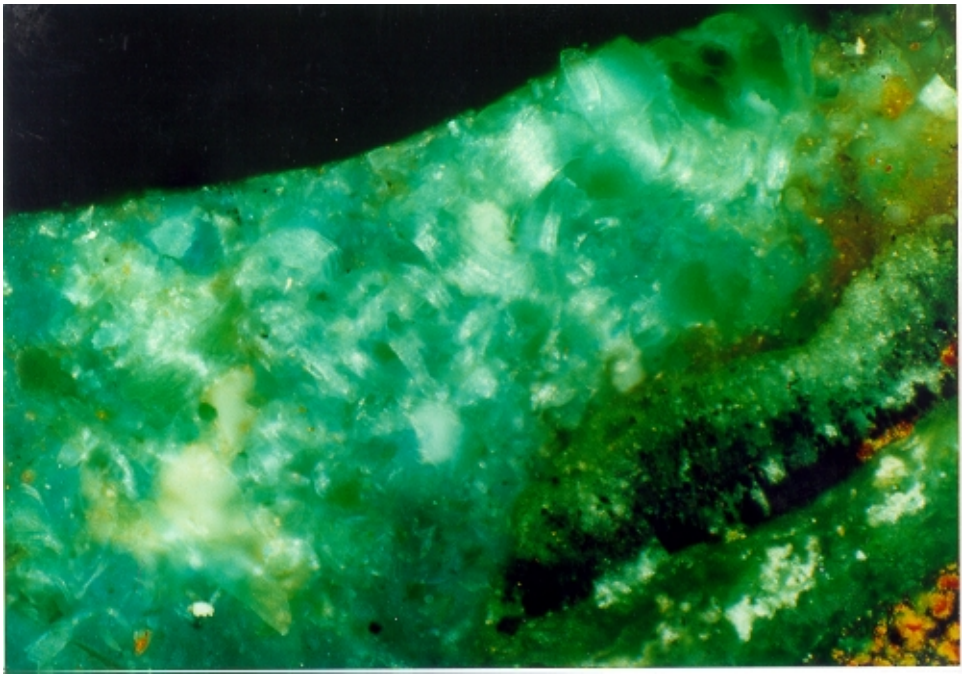


Fig. 6 Photomicrograph of fibrous malachite in corrosion overburden.
C/P. Width of the image = 0.7 mm.

**Microanalysis:**

EPMA spot analyses were carried out on the area of destannification (Fig. 7, corresponds to Fig. 4), the results are as follow:

| Point | Cu | Fe | Sn | Pb | S | Cl | Ag | Bi | As | Total |
|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 94.35 | 0.02 | 0.14 | 0.07 | 0.01 | 0.00 | 0.04 | 0.00 | 0.00 | 94.63 |
| **2** | 93.27 | 0.01 | 0.13 | 0.00 | 0.01 | 0.00 | 0.05 | 0.00 | 0.00 | 93.47 |
| **3** | 89.14 | 0.02 | 3.69 | 0.00 | 0.02 | 0.01 | 0.04 | 0.00 | 0.00 | 92.91 |
| **4** | 78.18 | 0.05 | 12.87 | 0.21 | 0.01 | 0.00 | 0.01 | 0.00 | 0.00 | 91.34 |
| **5** | 93.56 | 0.00 | 0.12 | 0.14 | 0.01 | 0.00 | 0.02 | 0.18 | 0.00 | 94.03 |
| **6** | 93.34 | 0.05 | 0.68 | 0.12 | 0.02 | 0.02 | 0.04 | 0.14 | 0.00 | 94.40 |

The concentration of Cu in the destannification area does not show a difference to that of redeposited Cu (checked in other samples). However, the backscattered electron image shows elemental contrast, which indicates uneven density of the copper.

EPMA linescans were carried out across the metallographic section; the results are shown in Fig. 8. The plot of concentration of Cu and Sn shows that Sn is only present in the metal and inner corrosion layers rather than outer corrosion layers. Its content is fairly constant. Fe and Cl are a few percent in an outer corrosion layer, which were from soil.

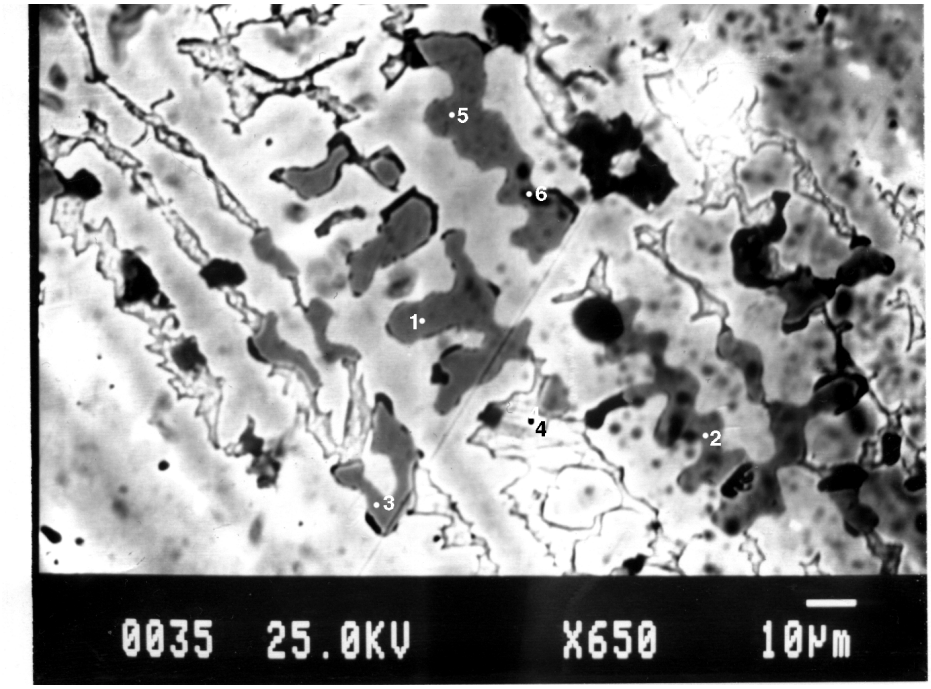



Fig. 7 BEI of destannificated Cu, showing EPMA points.

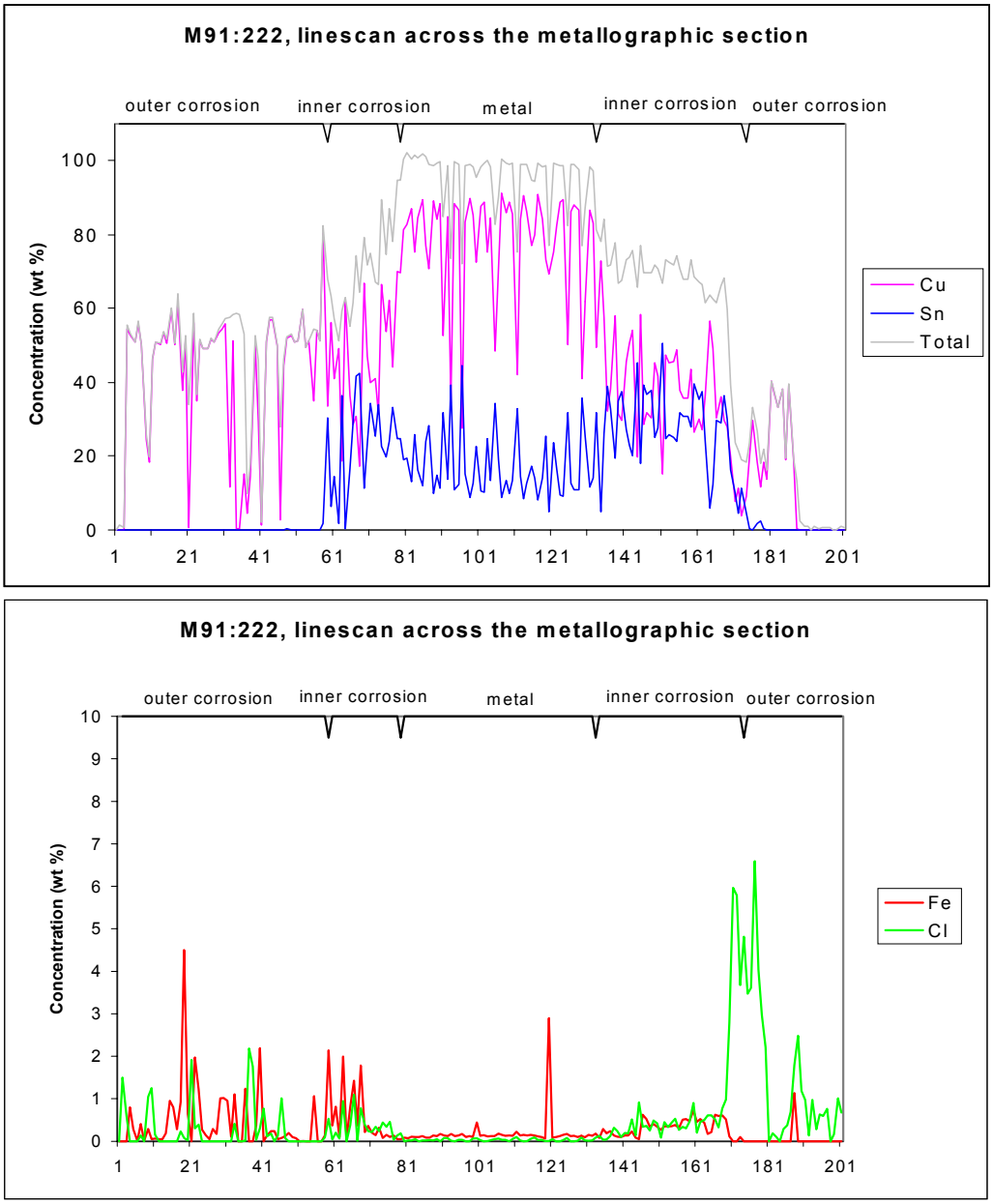



Fig. 8 EPMA linescan traversing cross section,
showing elemental distribution in different areas of the section.

## SUMMARY

It is a binary alloy of Cu-Sn with a dendritic structure. The best estimate of bulk composition determined by SEM/EDS is: 82% Cu and 17% Sn. It is deeply corroded. δ phases are partially corroded away inside the metal. Two types of corrosion, α-removal and δ-removal, are present on the surface. Destannification has occurred on this sample.

## GENERAL

**Object Number:** M91:400
**Object:** bell/*ling*
**Excavation Date:** 1994
**Date:** Late Western Zhou
**Origin:** Tianma-Qucun site
**Fragment Weight:** 4.5 g
**Fragment size:** 19x14x2.1 mm

**General description:**

This fragment has all sides broken. Corrosion index is 2. The surface is covered with green and blue corrosion products and soil. Cracks and holes can be seen in corrosion products. No decoration is apparent.

## TECHNICAL STUDIES OF METAL

**Metallographic structure:**

A section cut along the full width of the fragment was taken for metallographic observation. The original dimension is 2.1 mm as measured in the metallographic section. It has a cast dendritic structure with sulphide inclusions (Fig. 1). The average dendritic arm spacing is 0.016 mm. The sulphide inclusions in the uncorroded metal differ from sulphides in the corrosion (see below), which are comprised of Cu, S and Fe, regardless their morphologies (Fig. 1).

**Composition:**

**AAS:**

| Cu | Sn | Pb | Fe | As | Co | Zn | Ni | Ag | Au | Sb | Bi | total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ( | wt% | | ) | ( | | | ppm | | | | ) | (wt%) |
| 79.17 | 17.25 | 0.039 | 0.343 | nd | nd | 392 | 147 | 1225 | nd | nd | 1471 | 97.12 |

**Microanalysis:**

Several elemental linescans were carried out across sulphide inclusions. The results are shown in Fig. 2. EPMA measured Cu, S and Fe with quite constant content, which probably corresponds to that of $Cu_5FeS_4$. When the molten metal cooled down, Cu-rich $\alpha$ phase solidified first. Sulphide inclusions seem to have remained in Sn-rich solution and last solidified with eutectoid. This is identical with the metallography that most of sulphide inclusions are in eutectoids (Fig. 1).

**Microhardness:** 189Hv

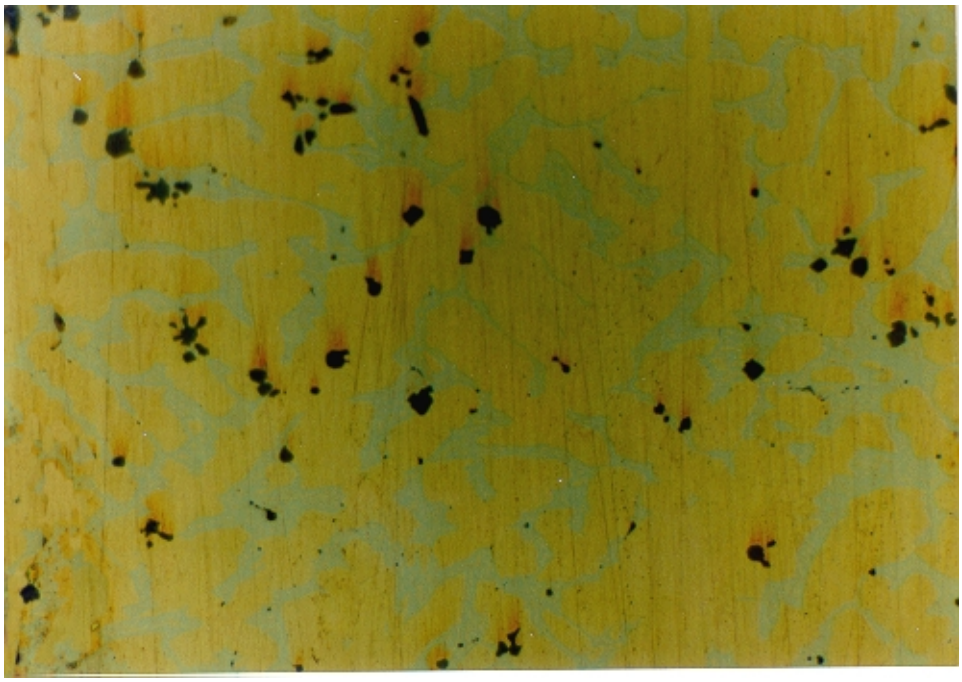


Fig. 1 Photomicrograph of dendritic microstructure showing sulphide inclusions (round or dendritic dark phases). Width of the image = 0.3 mm.

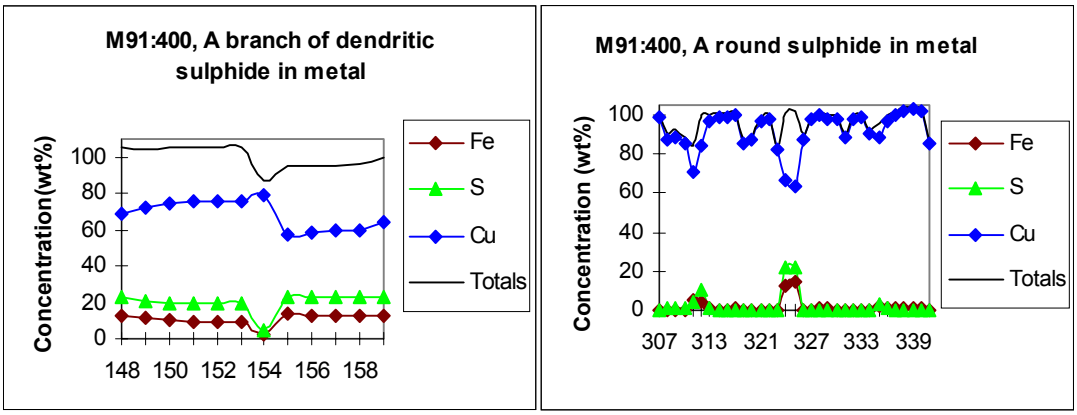



Fig. 2 EPMA linescan across sulphide inclusions.

## CORROSION

**XRD results:**

Surface sample: malachite, azurite.

Inner corrosion layer: cuprite, malachite, djurleite ($Cu_{1.97}S$).

**Metallographic observation:**

The original surfaces are well preserved. Sound metal can be seen in the middle. Corrosion developed on surfaces to the depth below the original surfaces in the range of 0.2-0.9 mm. Corrosion overburden is thin, with the thickest area being 0.3 mm.

Cracks can be seen penetrating the metal, filled with redeposited Cu (Fig. 3). Redeposited Cu is seen in δ-removal areas in the core (Fig. 4). Two types of corrosion: δ-removal (Fig. 4) and α-removal (Fig. 5) are seen in this sample. The former one is present inside the metal; while the later one is present on the surface.

The corrosion products from metal outwards are mixtures of cuprite and cassiterite (yellowish one); mixtures of cuprite, copper sulphide, and cassiterite (blackish one), mixtures of cuprite and copper sulphide (inner layer of corrosion overburden); and copper carbonates (outer layer of corrosion overburden)(Fig. 6). These mineral identifications are based on EPMA data and the characteristic colours in the metallographic section. The yellowish and blackish corrosion is within the original dimensions, in which δ phase can still be seen (Fig. 5). In the layer of mixtures of cuprite and copper sulphide, crystals with fractures are present, which is light grey in bright field, black in cross polars. EPMA data indicate that they are sulphide crystals.

**Microanalysis:**

Several EPMA linescans were carried out across the sulphide crystals, and the results are shown in Fig.7. Fig. 7 shows those sulphide crystals contain approximately 20% S and 80% Cu, which is similar to the ratio of $Cu_2S$. XRD indicates that they are djurleite ($Cu_{1.97}S$). SEM/EDS qualitatively analyses show that the black layer below the original surface is rich in Sn and S, which seems to be comprised of copper sulphides and cassiterite.

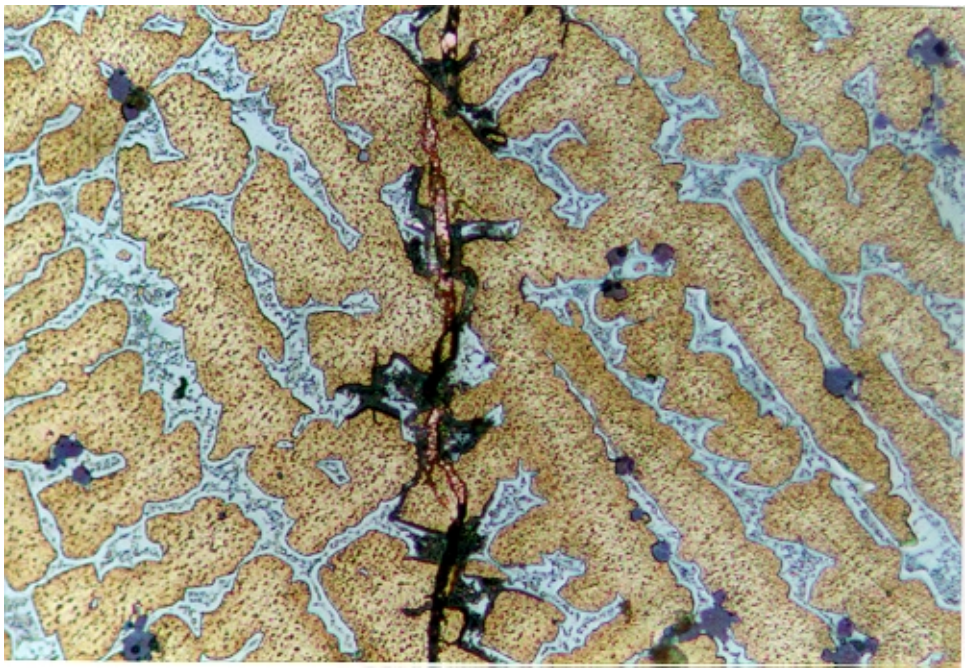


Fig. 3 Photomicrograph of redeposited Cu in a crack. Etched in aqueous $FeCl_3$.

BF. Width of the image = 0.2 mm.

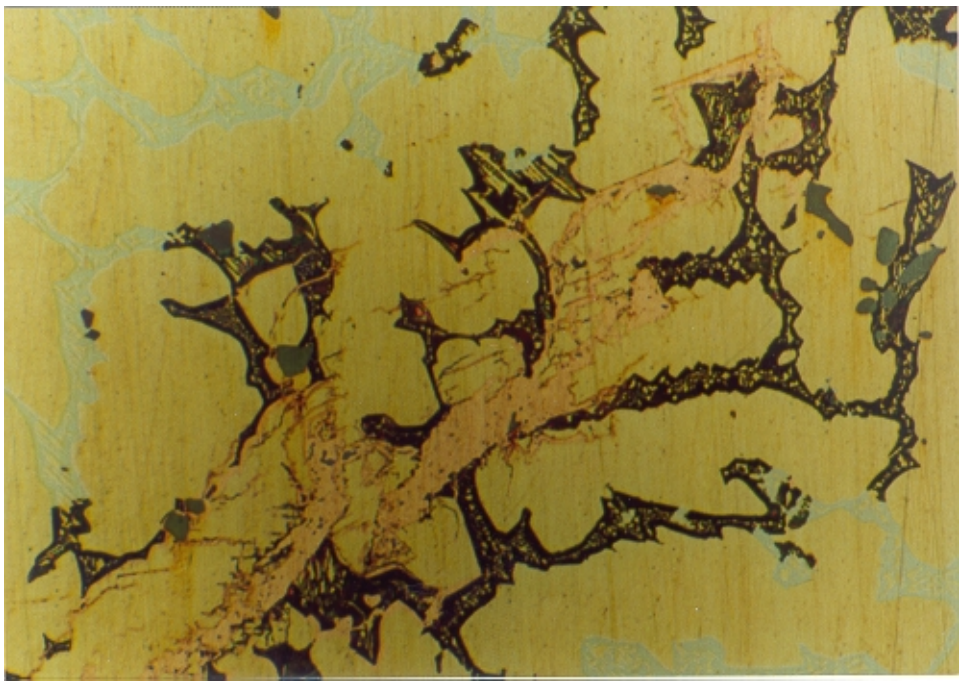


Fig. 4 Photomicrograph of δ-removal corrosion with redeposited Cu.

BF. Width of the image = 0.14 mm.

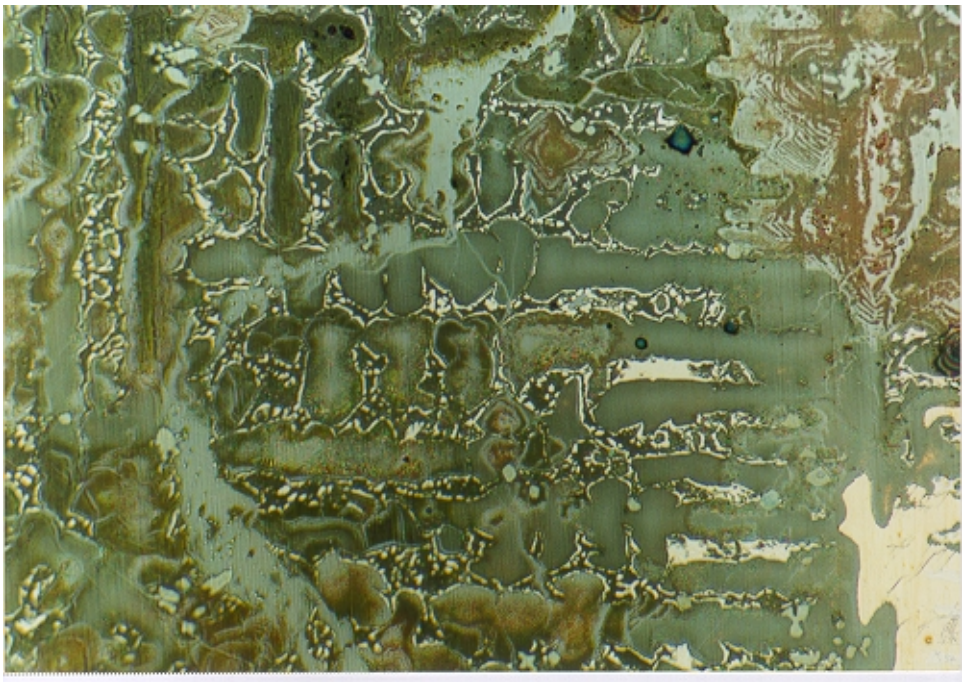


Fig. 5 Photomicrograph of α-removal corrosion.

BF. Width of the image = 0.28 mm.

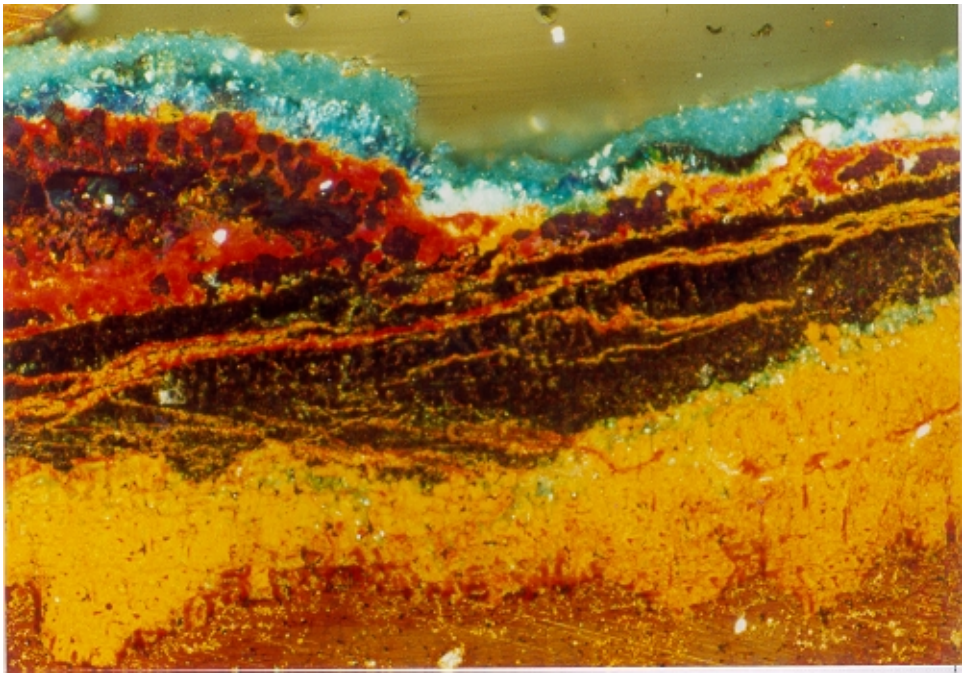


Fig. 6 Photomicrograph of corrosion on the surface.

The blackish crystals in the second outmost layer are copper sulphides

C/P. Width of the image = 0.7 mm.

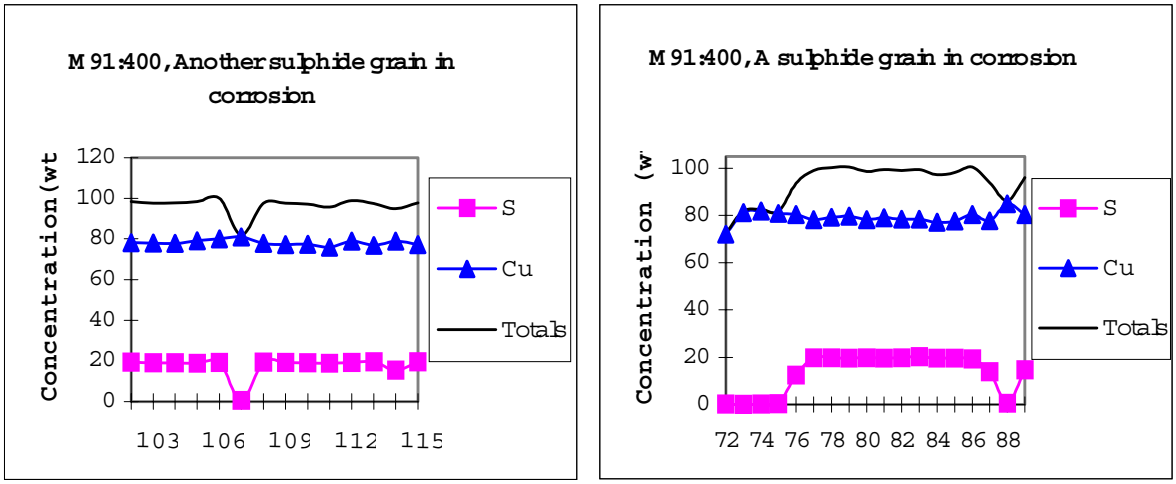



Fig.7 EPMA linescans across sulphide crystals in corrosion.

The areas of lower totals are probably cuprite based on the concentration of Cu.

## SUMMARY

It is a binary alloy of Cu-Sn with a cast dendritic structure. The bulk composition determined by AAS is 79.2% Cu and 17.3% Sn. There are sulphide inclusions, which are compounds of Cu, Fe and S. It is slightly corroded, with δ-removal and α-removal corrosion being present in different areas of the sample. Redeposited Cu is present inside the metal. A black layer is seen on the surface, sulphide crystals are present in the corrosion overburden.

## GENERAL

**Object Number:** M91:435
**Excavation Date:** 1994
**Origin:** Tianma-Qucun site

**Object:** vessel/plate
**Date:** Late Western Zhou
**Fragment Weight:** 0.8 g
**Fragment size:** 10x8x1.2-2.9 mm

**General description:**

This small fragment has all sides broken. Corrosion index is 5. There is a corrosion overburden, including blue, green and black corrosion products and soil. Fibrous corrosion can be seen. Decoration cavity is apparent on one surface (Fig. 1)

## TECHNICAL STUDIES OF METAL

**Metallographic structure:**

The estimated thickness is in the range of 1.4-2.9 mm as measured in the metallographic section. Most of this piece is nearly totally corroded, only a small area of 0.4x1.4 (mm) is partially corroded (the darker part on the left bottom corner of (Fig. 1). It has a cast dendrite structure (Fig. 2). The estimated dendritic spacing is 0.051 mm. The smooth lines of the decoration patterns indicate that they were cast in a mould rather than carved or engraved. The original surfaces can still be seen. There is a big cast pore in the middle (Fig. 1). Sulphide inclusions are seen in the metal.

**Composition:**

**AAS:** too corroded for analysis.

**Microanalysis:**

SEM/EDS semi-quantitative analysis was carried out on the least corroded area (600x), the result is as follows. It is a binary alloy of Cu-Sn.

| Cu | Sn | Fe | Total |
|---|---|---|---|
| 79.5 | 16.5 | 0.4 | 96.4 |

**Microhardness:** 143Hv

Fig. 1 Metallographic section, showing decoration cavity on outer surface, where there is a thick corrosion overburden. Metallic phases are only seen in a small area in the left bottom corner. Width of the image = 7mm.

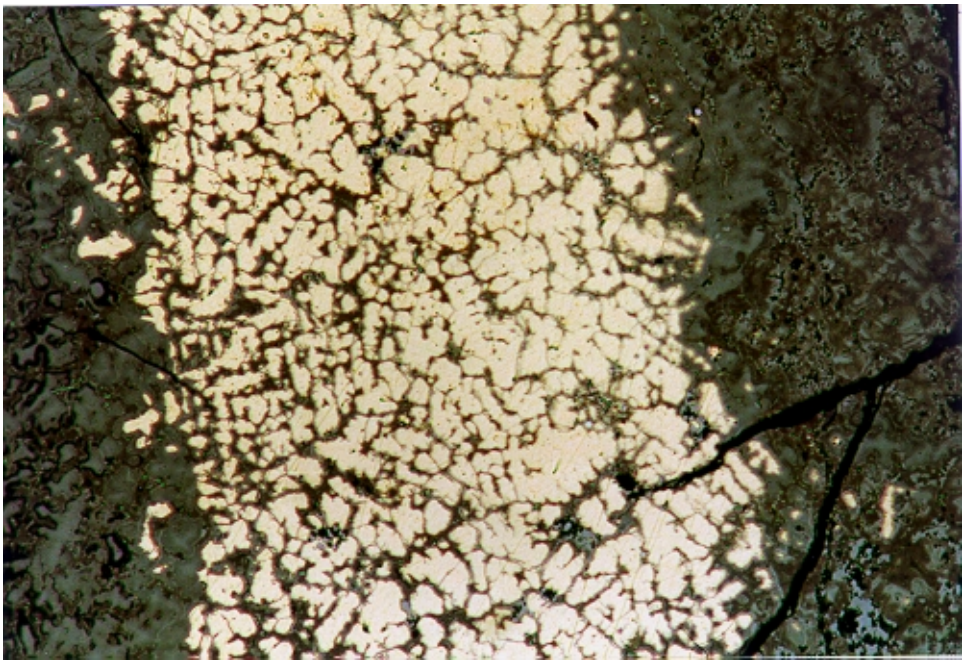


Fig. 2 Cast dendrite structure. BF. Width of the image = 1mm.

## CORROSION

**XRD results:**

Surface sample: malachite, cuprite, azurite

**Metallographic observation:**

Corrosion overburden on the decorated surface is thick, up to 0.7 mm. There are cuprite with cassiterite, sulphide with cuprite, malachite, and sulphide in sequence from the metal outwards (Fig. 3).

**Microanalysis:** not carried out

## SUMMARY

The presence of decoration patterns suggests this fragment was probably from a sidewall. It is a binary alloy of Cu-Sn with a dendritic structure. The best estimate of composition determined by SEM/EDS is 80% Cu and 17% Sn. Surface decoration was cast. Malachite and sulphide are the major corrosion products in the corrosion overburden.

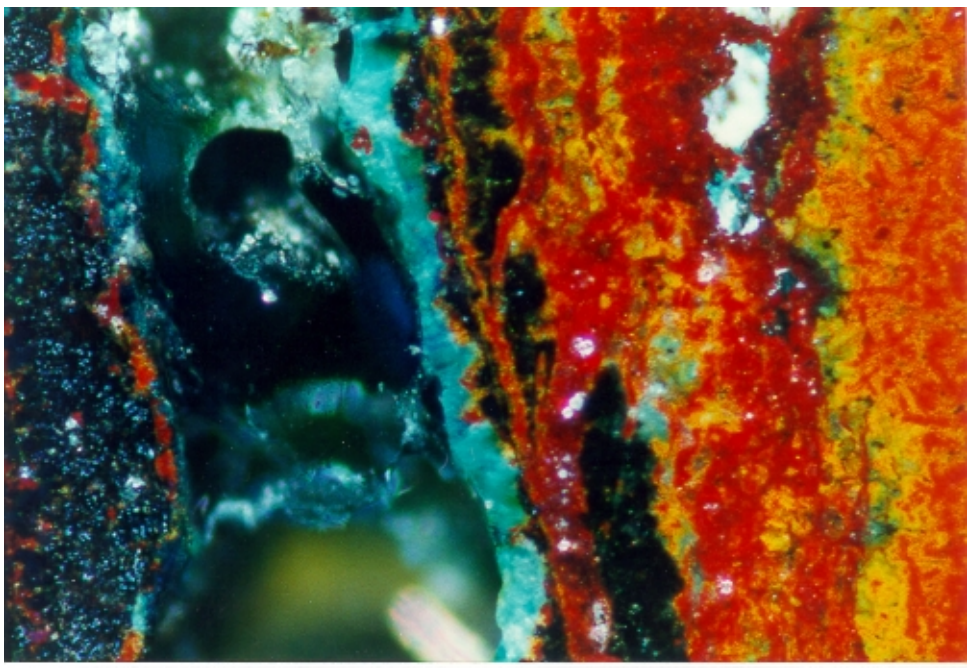


Fig. 3 Photomicrograph of corrosion overburden. C/P. Width of the image = 1mm.

## GENERAL

**Object Number:** M91:506A
**Excavation Date:** 1994
**Origin:** Tianma-Qucun site
**Object:** horse furniture/face ornament
**Date:** Late Western Zhou
**Fragment Weight:** 3.6 g
**Fragment size:** 18x14x1.2 mm

**General description:**

This fragment has all sides broken. Corrosion index is 5. There is a thick corrosion overburden, including green, light green and black corrosion products, and soil. Charcoal fragments are embedded in the corrosion. No decoration is apparent.

## TECHNICAL STUDIES OF METAL

**Metallographic structure:**

A section cut through the full width of the fragment was taken for metallographic observation. A pseudomorphic dendritic structure can still be seen although it is totally corroded (Fig. 1). The estimated original thickness is 1.2 mm as measured in the metallographic section. The estimated dendritic arm spacing is 0.107 mm.

**Composition:**

**AAS:** too corroded for analysis.

**Microanalysis:**

See corrosion section

**Microhardness:** too corroded for measuring.

Fig. 1 An entire surface showing a black layer. C/P. The thickness of the black layer ≈ 0.2 mm.

## CORROSION

### XRD results:

Inner corrosion layer: cuprite, malachite, azurite, brochantite, covellite.

### Metallographic observation:

It is totally corroded. Original surfaces can be identified on one side, but the layer is not clear on the other side. The corroded metal shows banded structures (Fig. 2).

There is a black layer (in C/P) between the corroded metal and the corrosion overburden on the outer surface (convex)(Fig. 1). It is quite even, with a thickness ranging from 170-250 μm. Its structure has no fundamental difference from the corroded metal: some δ phases are seen, some bluish light grey materials (in BF) are present in this layer, which are slightly different from cuprite in colour (Fig. 3). A layer of cuprite is beneath the black layer, which is next to the metal.

The corrosion overburden is up to 0.64 mm thick as measured in the metallographic section. Corrosion products are identified as malachite, cuprite, cassiterite, and copper sulphide based on microanalysis and characteristic colour in the metallographic section. Copper sulphide crystals show different colours (Fig. 4). Particles of redeposited Cu are seen in cuprite, both in corroded metal and in corrosion overburden.

### Microanalysis:

SEM/EDS semi-quantitative analysis was carried out on both corroded metal and the black layer; the results are as follows. It is a binary alloy of Cu-Sn. Fe and S is richer in the black layer than that in metal.

Corroded metal:

| **Cu** | **Sn** | **Fe** | **S** | **Si** | **Cl** | **Total** |
|---|---|---|---|---|---|---|
| 47.6 | 17.6 | 0.7 | 1.0 | 0.6 | 0.5 | 68.0 |

Black layer:

| **Cu** | **Sn** | **Fe** | **S** | **Si** | **Total** |
|---|---|---|---|---|---|
| 33.8 | 20.2 | 1.3 | 5.1 | 0.5 | 60.9 |

SEM analysis proves that crystals with fractures in corrosion overburden are copper sulphide (Fig. 4), and different colour represents difference in sulphur content: the

darker the colour, the more the sulphur. For example, white colour of a crystal contains 73.3% Cu and 26.0% S (similar to $Cu_2S$, chalcocite), light blue one contains 67.7% Cu and 31.2% S, and blue one contains 65.3% Cu and 34.2% S (similar to CuS, covellite).

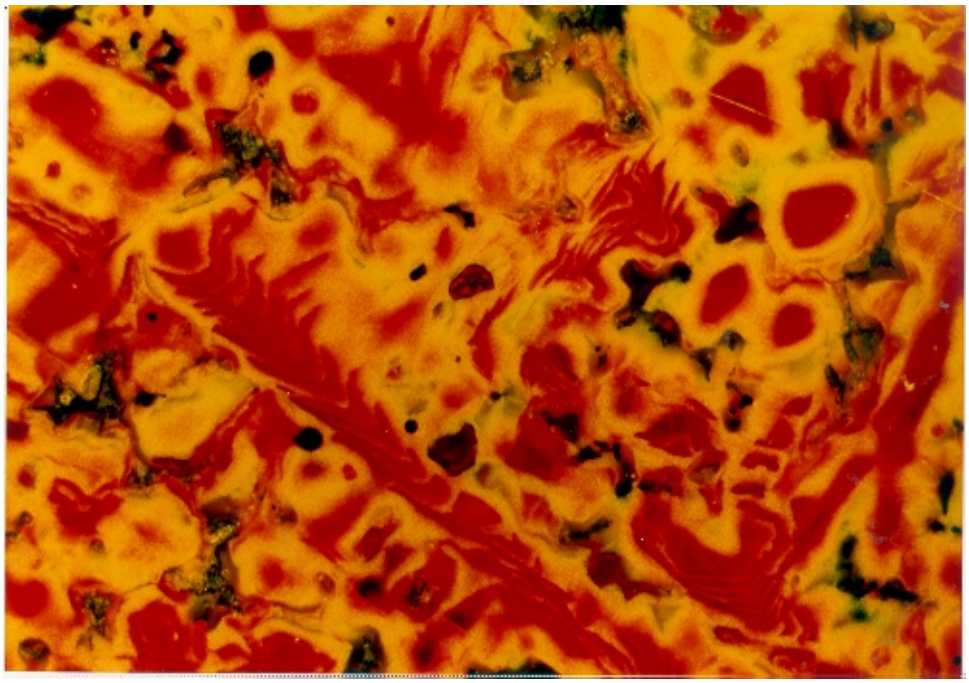


Fig. 2 Photomicrograph of banded structure. The red part is rich in Cu, the yellow part rich in Sn. C/P. Width of the image = 0.9 mm.

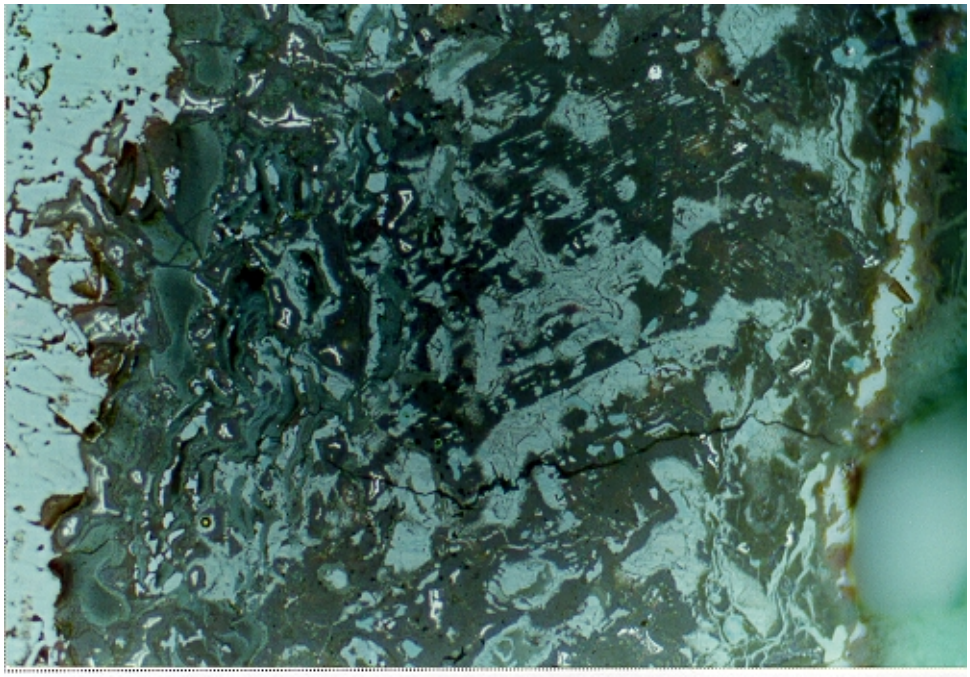


Fig. 3 Photomicrograph of the black layer showing copper sulphides.
BF. Width of the image = 0.4 mm.

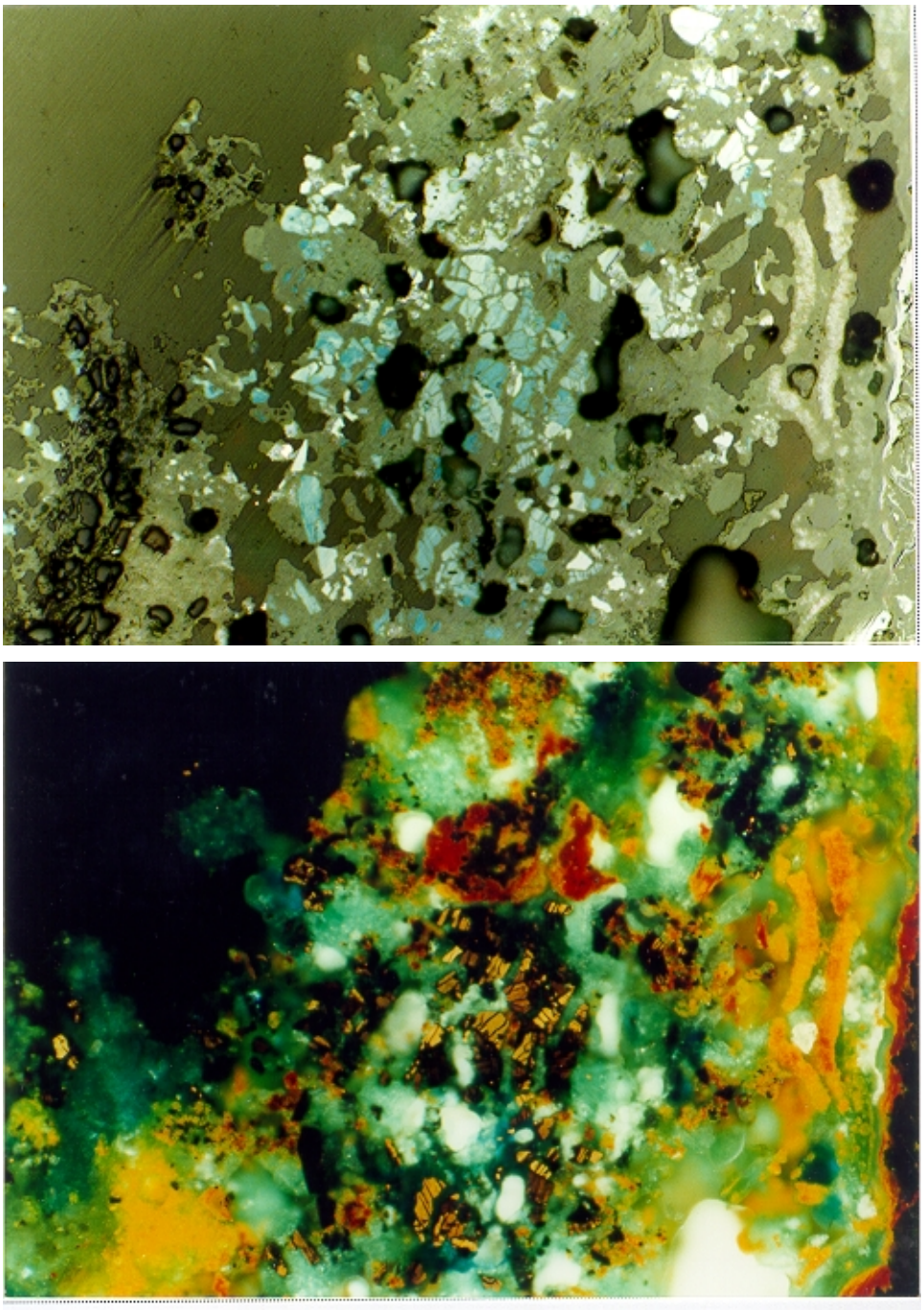


Fig. 4 Photomicrograph of sulphide crystals in corrosion overburden.
Width of the image = 0.7 mm. Top: BF; Bottom: C/P.

Colour maps have been carried out on the surface using SEM/EDS (Fig. 5). It shows the enrichment of sulphur in the black layer and the crystals in the corrosion overburden.

EPMA point analyses have been carried out on the banded area of Fig. 2. The reddish areas of the banded structures are rich in Cu, and the yellowish areas are rich in Sn, which can be assumed a mixed corrosion of Cu and Sn, i.e. cuprite and cassiterite.

EPMA linscane was carried out across the section, the results are plotted as Fig. 6. Some observations can be outlined from Fig. 6:

- Arsenic is present in both black layer and corroded metal but not the cuprite layer. Maximum As found in this sample is 9.21% presented in the black layer. There is more arsenic in the black layer than in the corroded metal.
- Compared to the corroded metal, the black layer is rich in Sn, Fe, Pb and S. There is a correlation between concentration of Sn and Fe, with Fe increasing with Sn. So is the correlation of Sn and Fe in the corroded metal, but with lower contents. Lead is lower than 0.5% in all detected points. Sulphur is higher in the black layer than in the corroded metal, and is associated with Cu, which increases with Cu.
- Cuprite layer separates the black layer and the metal. It is relatively pure, in which only chloride (up to 1.76%) is higher than that in the corroded metal, Chloride is absent in the black layer (no more than 0.04% Cl).
- Hg was detected in the whole cross section, with maximum content being 0.24%. Examination of Hg of this sample using EMPA did not show any concentration difference between the black layer and the corroded metal. Therefore, it is not convincing that Hg was from tinning process. Hg probably came from cinnabar placed in the tomb.

**SUMMARY**

It is a binary alloy of Cu-Sn with a dendritic structure based on the metallographic observations and microanalysis. The original composition is not estimated, because it is totally corroded. Copper sulphide crystals are present in corrosion overburden. There is a black layer on the surface. Redeposited Cu is seen within cuprite, both in the corroded metal and in the corrosion overburden.

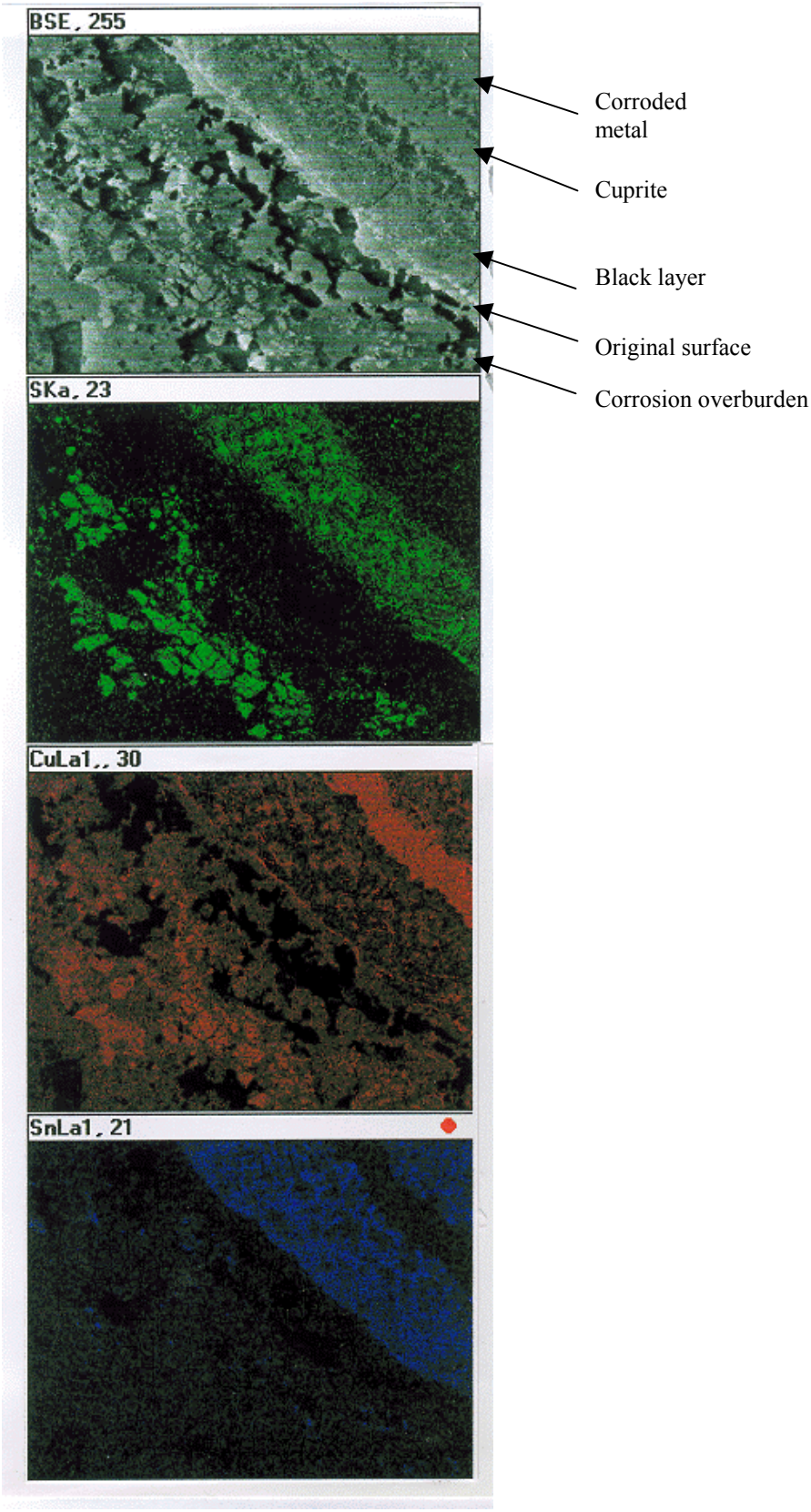



Fig. 5 SEM/EDS colour maps of Cu, S, Sn on the surface,
showing enrichment of sulphur in the black layer and corrosion overburden.

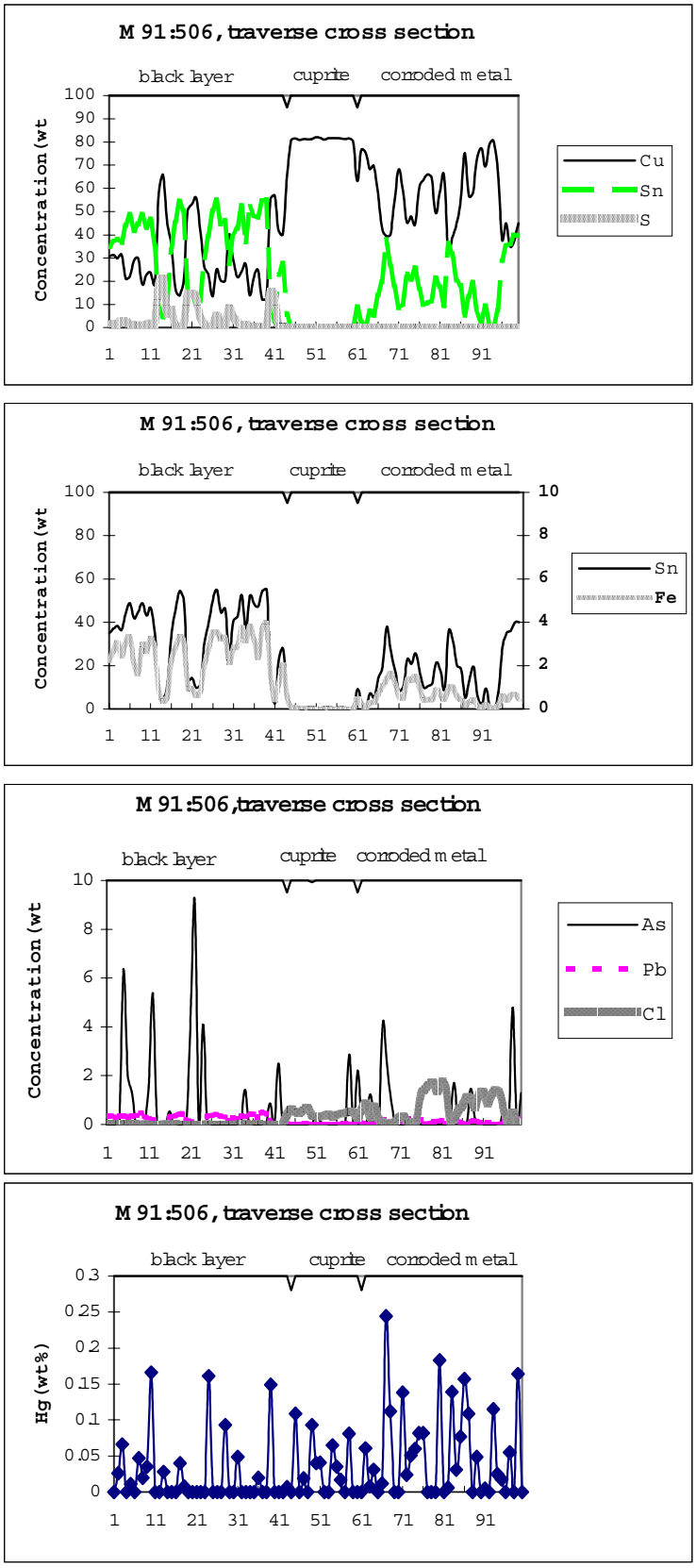



Fig. 6 EPMA linescan across metallographic section

## GENERAL

**Object Number:** M91:506B
**Excavation Date:** 1994
**Origin:** Tianma-Qucun site
**Object:** horse fitting/face ornament
**Date:** Late Western Zhou
**Fragment Weight:** 3.6 g
**Fragment size:** 18x14x? mm

**General description:**

This fragment is thought to be from the same object as M91:506A by the excavators. It looks like a piece of corrosion product rather than a metal, because it is very light and porous.

## TECHNICAL STUDIES OF METAL

**Metallographic structure:**

It is totally corroded. The original surfaces can not be identified, so the original thickness is not estimated. A needle-like structure can be seen in metallography (Fig. 1).

**Composition:**

**AAS:** too corroded for analysis.

**Microanalysis:**

Needle structure can be seen clearly through both secondary and backscattered electron images with EPMA (Fig. 2). The two-phase structure, and grain boundaries can be seen. These lines within grains are too evenly aligned to be corroded slip lines. EPMA linescan from A to B across a grain (in Fig. 2) (1μm interval, 46 steps) shows a little variation of concentration of Cu and Sn (Table1). The atomic ratio of Sn to Cu is quite constant, in the range of 2.8 - 3.3. The content of Fe and Pb is also quite constant. Arsenic is present in a few points, with highest one being 7.1%. It is difficult to estimate its original composition due to corrosion.

The corroded structure along with microanalysis result suggests that it was a two-phases, possibly α and β, alloy of Cu-Sn. The original composition could have been in the range of α+β region, i.e.13.5-25.5% Sn, of the diagram. α phases were solidified first, then the peritectic reaction giving rise to precipitation of β phase

occurred when temperature dropped to 799°C. The remnant grain boundaries of α phase indicates that the transition from α phase to β phase must have not been completed. The presence of β phase suggests that this piece had been quenched at above 520°C, because there was no δ phase observed. Another interpretation could be Widmanstätten separation (β phase resulted from the existing α phase) (Per. Comm. Dr. Charles). The possibility of quench can not be ruled out by this interpretation due to the presence of β phase. It could also be the result of working, i.e. cast – worked – annealed – worked.

**Microhardness:** too corroded for measuring.

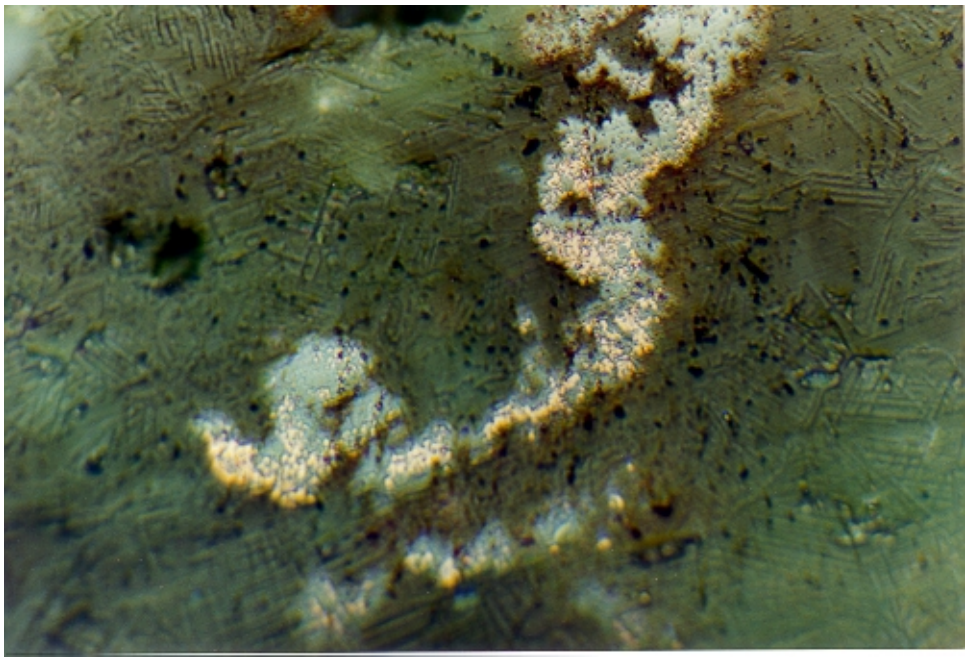


Fig. 1 Microstructure of corroded metal, showing needle-like structure and redeposited Cu. BF. Width of the image = 0.2 mm.

## CORROSION

### XRD results:

Tiny piece ground to a powder: malachite, azurite, quartz, cuprite, iron sulphate hydrate.

### Metallographic observation:

Redeposited Cu is seen in cuprite within the corroded metal (Fig. 1). Corrosion overburden is comprised of malachite, including fibrous type, sulphide and soil identified by their characteristic colours in the metallographic section.

### Microanalysis:

EPMA was carried out on three light grains (in backscattered electron image) in the corrosion overburden; the results are as follows (Fig. 3):

| point | Cu | Fe | Sn | Pb | S | Cl | Ag | Bi | As | Total |
|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 2.41 | 2.93 | 31.64 | 0.64 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 37.63 |
| **2** | 55.67 | 0.05 | 0.13 | 0.00 | 15.45 | 0.00 | 0.41 | 0.22 | 8.82 | 80.75 |
| **3** | 10.81 | 3.00 | 26.32 | 0.73 | 0.07 | 0.02 | 0.00 | 0.37 | 0.00 | 41.32 |

## SUMMARY

It is 2-phases structure with grain boundaries and needles within the grains. It is not completely clear what the original composition was and how the structure was finally formed. Based on its microstructure this piece is unlikely to be from the same object as M91:506A. It is also unlikely to be from the same object but different part made separately from the fragment of M91:506A, since horse furniture/face ornament is a small object and would have been integrate cast rather than a composite cast.

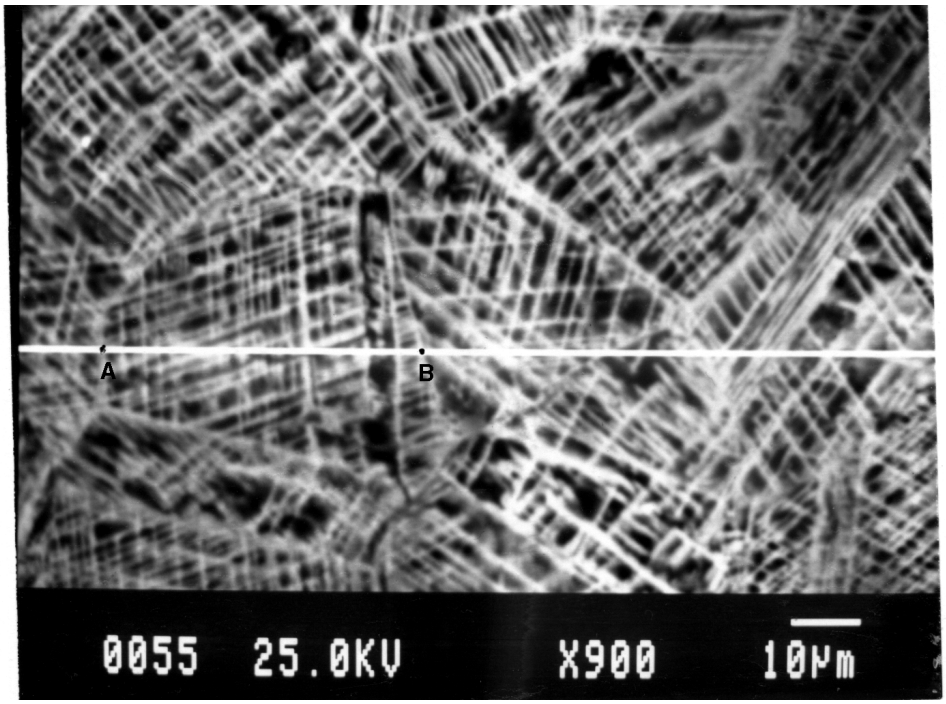



Fig. 2 BEI of corroded metal, showing needle-like structure within grains. The result of EPMA linescan from A to B is listed in Table 1.

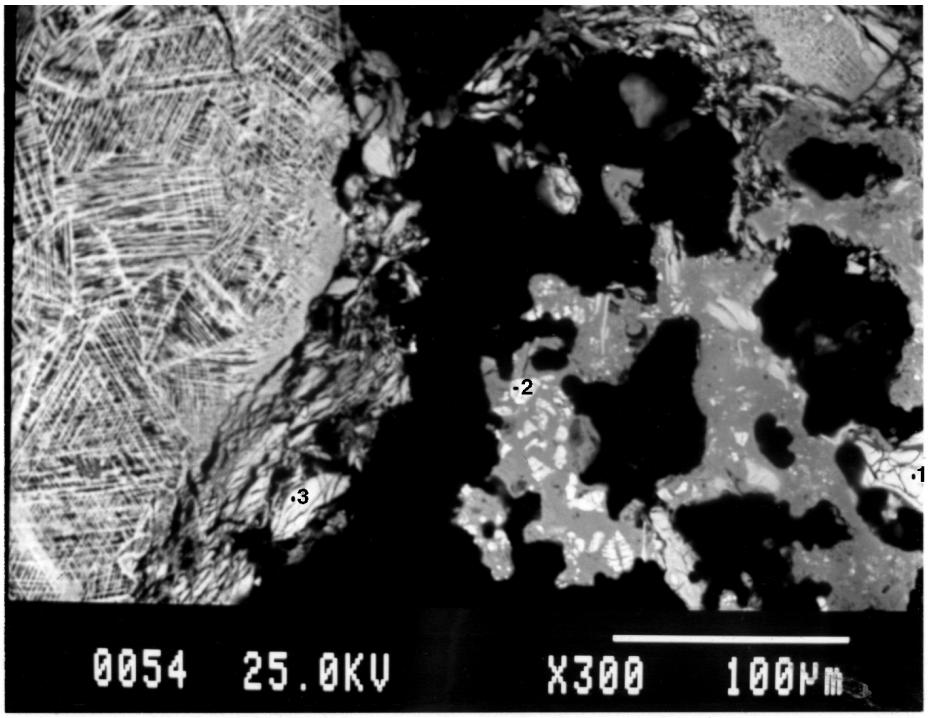



Fig. 3 BEI of corrosion overburden, showing EPMA points.

Table 1. The results of EPMA linescan across a grain from A to B (Fig. 2)

| No. | Cu | Fe | Sn | Pb | Bi | As | Total | Sn/Cu (atomic ratio) |
|---|---|---|---|---|---|---|---|---|
| 1 | 7.30 | 1.61 | 39.03 | 1.33 | 0.23 | 3.36 | 52.86 | 2.86 |
| 2 | 7.20 | 1.78 | 40.75 | 1.24 | 0.30 | 1.75 | 53.02 | 3.03 |
| 3 | 7.81 | 1.92 | 42.52 | 1.39 | 0.11 | 0.00 | 53.74 | 2.92 |
| 4 | 7.02 | 1.85 | 42.59 | 1.56 | 0.32 | 2.74 | 56.08 | 3.25 |
| 5 | 7.07 | 1.89 | 42.68 | 1.53 | 0.16 | 0.79 | 54.11 | 3.23 |
| 6 | 7.88 | 2.12 | 44.20 | 1.70 | 0.18 | 0.00 | 56.08 | 3.00 |
| 7 | 7.80 | 2.07 | 45.35 | 1.72 | 0.19 | 0.08 | 57.19 | 3.11 |
| 8 | 7.83 | 2.13 | 43.30 | 1.62 | 0.14 | 0.00 | 55.01 | 2.96 |
| 9 | 8.08 | 2.18 | 45.37 | 1.64 | 0.34 | 1.88 | 59.49 | 3.01 |
| 10 | 8.24 | 2.26 | 46.65 | 1.92 | 0.24 | 0.66 | 59.97 | 3.03 |
| 11 | 7.49 | 1.93 | 42.10 | 1.56 | 0.29 | 0.00 | 53.37 | 3.01 |
| 12 | 7.27 | 1.88 | 41.69 | 1.43 | 0.15 | 1.48 | 53.90 | 3.07 |
| 13 | 7.51 | 1.87 | 41.82 | 1.32 | 0.24 | 0.00 | 52.76 | 2.98 |
| 14 | 7.80 | 2.03 | 40.88 | 1.30 | 0.17 | 0.00 | 52.18 | 2.81 |
| 15 | 7.53 | 1.95 | 42.74 | 1.73 | 0.25 | 0.00 | 54.20 | 3.04 |
| 16 | 7.89 | 2.06 | 41.58 | 1.33 | 0.20 | 0.00 | 53.07 | 2.82 |
| 17 | 7.39 | 1.84 | 39.32 | 1.14 | 0.14 | 0.00 | 49.82 | 2.85 |
| 18 | 7.59 | 1.95 | 39.80 | 1.26 | 0.06 | 0.00 | 50.66 | 2.81 |
| 19 | 7.48 | 1.94 | 40.81 | 1.39 | 0.11 | 0.00 | 51.73 | 2.92 |
| 20 | 7.44 | 1.67 | 40.03 | 1.32 | 0.15 | 1.03 | 51.64 | 2.88 |
| 21 | 6.91 | 1.52 | 40.10 | 1.47 | 0.14 | 1.11 | 51.25 | 3.11 |
| 22 | 7.30 | 1.67 | 41.45 | 1.57 | 0.18 | 0.25 | 52.41 | 3.04 |
| 23 | 7.13 | 1.69 | 37.97 | 1.08 | 0.17 | 0.00 | 48.04 | 2.85 |
| 24 | 7.38 | 1.87 | 40.26 | 1.31 | 0.16 | 1.53 | 52.50 | 2.92 |
| 25 | 7.77 | 1.95 | 39.08 | 1.12 | 0.25 | 0.00 | 50.16 | 2.69 |
| 26 | 7.82 | 2.03 | 39.33 | 1.19 | 0.16 | 0.00 | 50.52 | 2.69 |
| 27 | 6.94 | 1.78 | 39.73 | 1.33 | 0.18 | 1.96 | 51.92 | 3.06 |
| 28 | 7.15 | 1.89 | 40.46 | 1.42 | 0.16 | 0.00 | 51.09 | 3.03 |
| 29 | 7.31 | 1.95 | 39.40 | 1.32 | 0.16 | 0.00 | 50.14 | 2.89 |
| 30 | 7.52 | 1.60 | 41.17 | 1.51 | 0.52 | 2.32 | 54.63 | 2.93 |
| 31 | 6.46 | 1.61 | 36.40 | 1.31 | 0.23 | 0.60 | 46.61 | 3.02 |
| 32 | 6.14 | 1.59 | 31.92 | 1.04 | 0.08 | 0.00 | 40.77 | 2.78 |
| 33 | 5.64 | 1.39 | 29.16 | 0.81 | 0.37 | 0.17 | 37.54 | 2.77 |
| 34 | 5.93 | 1.52 | 30.78 | 0.95 | 0.39 | 1.31 | 40.88 | 2.78 |
| 35 | 7.19 | 1.63 | 41.53 | 1.43 | 0.44 | 7.10 | 59.32 | 3.09 |
| 36 | 7.22 | 1.65 | 40.88 | 1.45 | 0.15 | 0.00 | 51.36 | 3.03 |
| 37 | 7.43 | 1.78 | 41.28 | 1.38 | 0.22 | 0.00 | 52.08 | 2.97 |
| 38 | 7.85 | 1.67 | 43.30 | 1.43 | 0.48 | 0.00 | 54.73 | 2.95 |
| 39 | 6.56 | 1.70 | 38.41 | 1.40 | 0.20 | 0.00 | 48.27 | 3.14 |
| 40 | 6.70 | 1.68 | 38.50 | 1.39 | 0.13 | 0.00 | 48.40 | 3.08 |
| 41 | 7.04 | 1.78 | 39.84 | 1.44 | 0.20 | 0.00 | 50.29 | 3.03 |
| 42 | 7.24 | 1.69 | 41.51 | 1.68 | 0.35 | 0.00 | 52.47 | 3.07 |
| 43 | 6.86 | 1.60 | 40.23 | 1.45 | 0.31 | 3.23 | 53.69 | 3.14 |
| 44 | 7.23 | 1.75 | 41.86 | 1.38 | 0.29 | 0.00 | 52.50 | 3.10 |
| 45 | 7.65 | 1.63 | 43.87 | 1.65 | 0.21 | 0.00 | 55.01 | 3.07 |
| 46 | 7.70 | 1.63 | 44.43 | 1.67 | 0.33 | 0.00 | 55.76 | 3.09 |

## GENERAL

**Object Number:** M91:unknown
**Excavation Date:** 1994
**Origin:** Tianma-Qucun site

**Object:** unknown
**Date:** Late Western Zhou
**Fragment Weight:** 1.2 g
**Fragment size:** 12x7x1.1-1.9 mm

**General description:**

There is no soil and thick corrosion overburden on this fragment. Corrosion index is 3. No decoration is apparent (Fig.1)

## TECHNICAL STUDIES OF METAL

**Metallographic structure:**

The estimated original thickness is 1.1-1.9 mm as measured in the metallographic section. It has an equi-axed structure (Fig. 2). The estimated grain size is 0.016 mm. Fe inclusions can be seen in α grains (light blue dots in Fig. 2). Sulphide inclusions are seen on the grain boundaries (bluish grey dendrite or round shapes).

**Composition:**

**AAS:** too corroded for analysis

**Microanalysis:**

SEM/EDS semi-quantitative analysis was carried out on the least corroded area (860x), the result is as follows. It is a binary alloy of Cu-Sn with inclusions of Fe and S.

| Cu | Sn | Fe | S | Total |
|---|---|---|---|---|
| 83.7 | 10.3 | 1.3 | 0.5 | 95.8 |

**Microhardness:** 122Hv

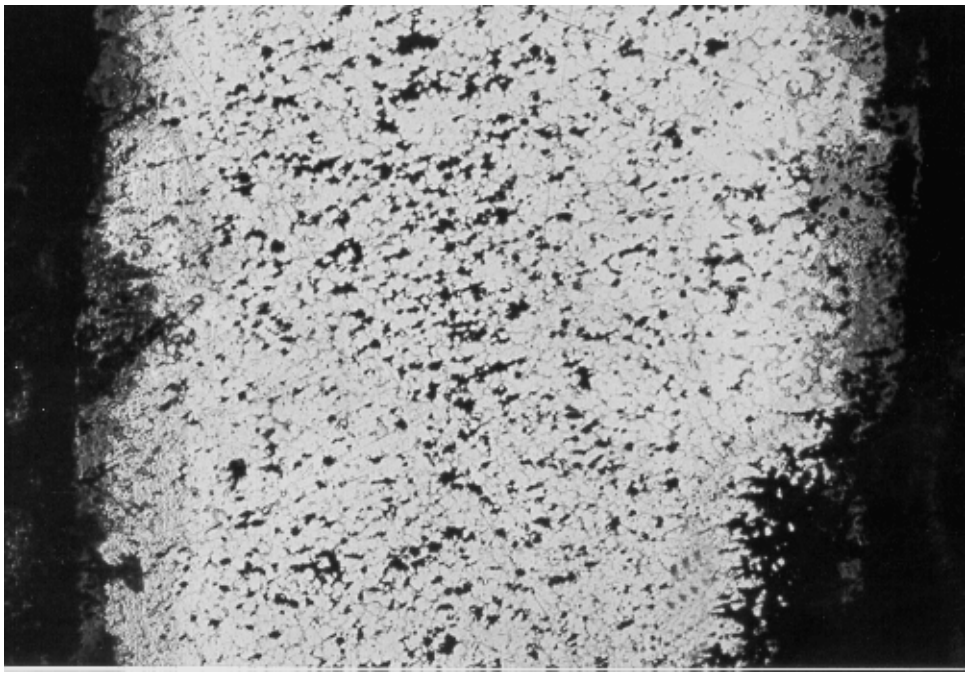


Fig. 1 Metallographic section. BF. Width of the image = 2 mm.

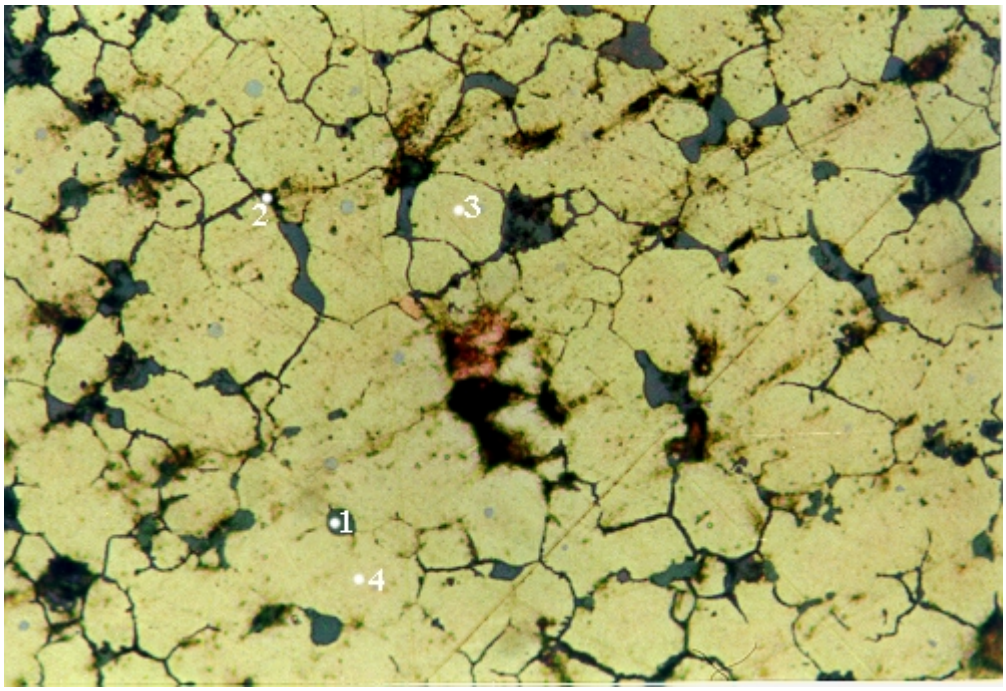



Fig. 2 Photomicrograph of equi-axed structure, showing EPMA points.
BF. Width of the image = 0. 2mm.

## CORROSION

**XRD results:** not carried out.

### Metallographic observation:

The original surfaces are disrupted in some areas, many corrosion pits are seen (Fig. 1). Corrosion follows grain boundaries (Fig. 2). In the surface disrupted area, corrosion is deep, with a few isolated α grains remaining (Fig. 3). Redeposited Cu is seen inside the metal and on the surface (Fig. 4).

### Microanalysis:

EPMA spot analysis was carried out on both the metal (Fig. 2) and the surface disrupted area (Fig. 3); the results are listed below.

| Point | Description |
|---|---|
| **1** | Copper sulphide |
| **2** | Corrosion pit in metal core |
| **3, 4** | α phase |
| **5, 8** | Corrosion pit on the disrupted surface |
| **6** | Intergranular corrosion |
| **7** | α on the disrupted surface |
| **9** | Redeposited Cu within cuprite |

| Point | Cu | Fe | Au | Ni | Sn | Pb | Zn | Ag | Hg | As | Sb | Bi | Co | S | Cl | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 73.07 | 0.61 | 0.08 | 0.00 | 2.96 | 0.00 | 0.00 | 0.06 | 0.00 | 0.00 | 0.00 | 0.09 | 0.01 | 12.83 | 0.13 | 89.83 |
| **2** | 54.26 | 0.88 | 0.00 | 0.01 | 17.01 | 0.00 | 0.00 | 0.10 | 0.08 | 0.00 | 0.00 | 0.01 | 0.01 | 0.16 | 0.25 | 72.76 |
| **3** | 87.67 | 1.84 | 0.00 | 0.02 | 8.92 | 0.01 | 0.00 | 0.06 | 0.05 | 0.00 | 0.00 | 0.02 | 0.02 | 0.01 | 0.00 | 98.61 |
| **4** | 87.94 | 2.42 | 0.00 | 0.04 | 6.85 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.05 | 0.02 | 0.00 | 97.33 |
| **5** | 48.75 | 2.05 | 0.07 | 0.01 | 18.23 | 0.31 | 0.02 | 0.00 | 0.21 | 0.00 | 0.00 | 0.02 | 0.00 | 0.38 | 11.26 | 81.29 |
| **6** | 51.25 | 2.29 | 0.04 | 0.00 | 19.16 | 0.18 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.05 | 0.00 | 0.39 | 3.43 | 76.77 |
| **7** | 89.49 | 2.18 | 0.07 | 0.03 | 6.37 | 0.04 | 0.00 | 0.04 | 0.06 | 0.00 | 0.00 | 0.00 | 0.04 | 0.00 | 0.00 | 98.30 |
| **8** | 66.03 | 0.04 | 0.06 | 0.00 | 0.05 | 0.00 | 0.00 | 0.08 | 0.09 | 0.01 | 0.00 | 0.00 | 0.01 | 0.05 | 25.18 | 91.61 |
| **9** | 94.99 | 0.00 | 0.01 | 0.00 | 0.01 | 0.02 | 0.00 | 0.07 | 0.03 | 0.08 | 0.01 | 0.00 | 0.00 | 0.14 | 0.00 | 95.38 |

EPMA indicates that the surface is disrupted by chloride, it is hard to precisely identify the chloride, nantokite or bronze disease based on the ratio of Cu/Cl alone. According to its appearance in metallography, it is likely to be nantokite.

## SUMMARY

It is a binary alloy of Cu-Sn with an equi-axed structure. There are Fe and S inclusions. The best estimate of composition conducted by SEM/EDS is 84% Cu, 10% Sn, 1.3% Fe and 0.5% S. Corrosion follows grain boundaries. The original surfaces were disrupted by chlorides. Redeposited Cu is seen both inside the metal and on the surface.

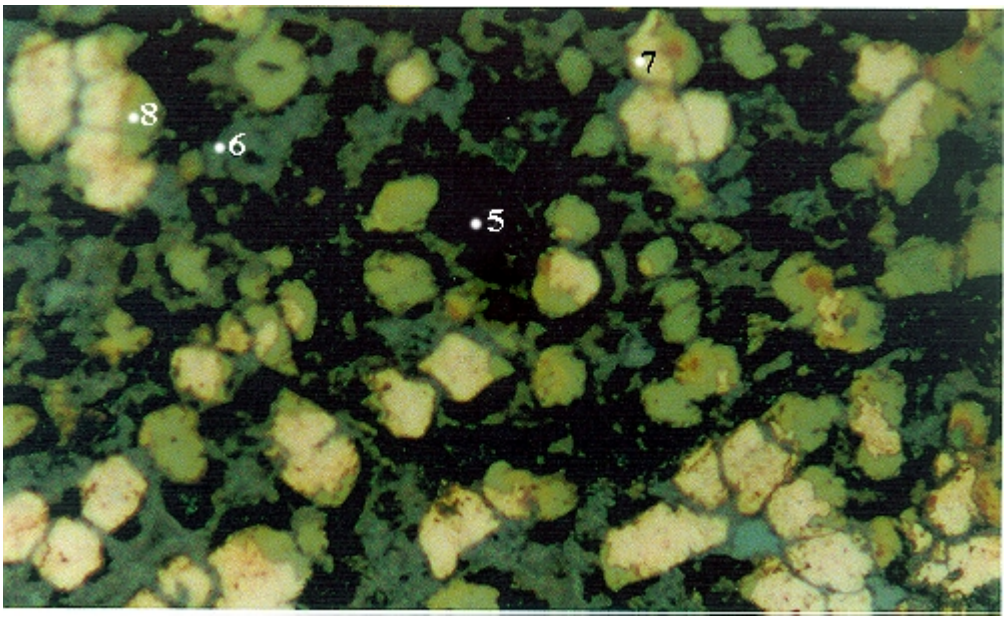



Fig. 3 Photomicrograph of chloride presence area, showing EPMA points. BF. Width of the image = 0.2 mm.

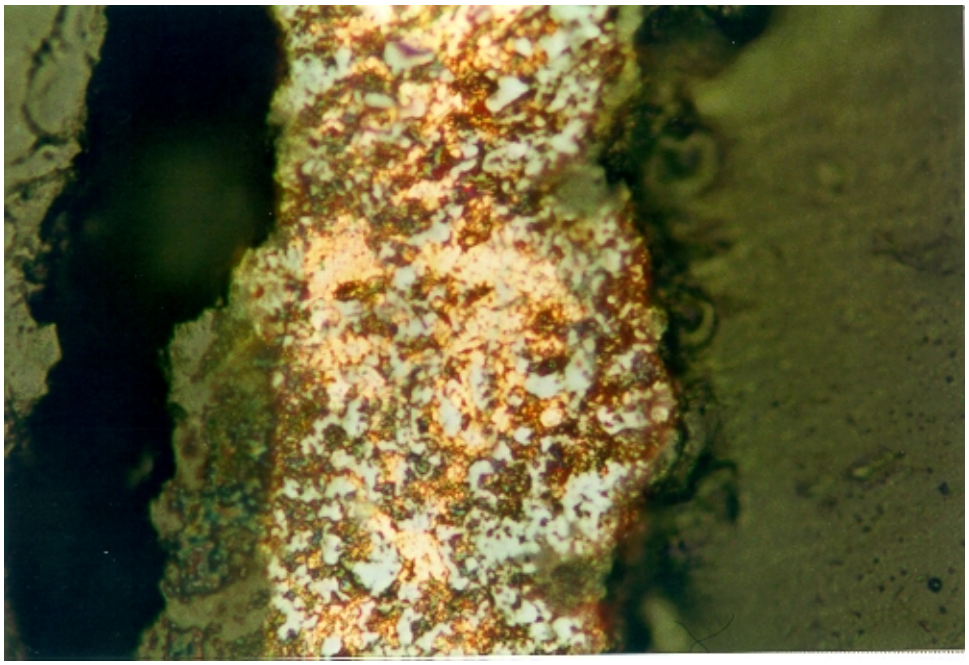


Fig. 4 Photomicrograph of redeposited Cu within cuprite. BF. Width of the image = 0.2 mm.

## GENERAL

**Object Number:** M63:81
**Excavation Date:** 1994
**Origin:** Tianma-Qucun site

**Object:** vessel/*hu*
**Date:** Late Western Zhou
**Fragment Weight:** 0.9 g
**Fragment size:** 9x7x2.1 mm

**General description:**

This fragment has deep corrosion but a thin corrosion overburden, including green corrosion products and soil. Soil is predominant on the inner surface (slightly concave), while green corrosion product is dominant on the outer surface (slightly convex). Corrosion index is 4. No decoration is apparent.

## TECHNICAL STUDIES OF METAL

**Metallographic structure:**

Although the original surfaces are well preserved, uncorroded metal remains only in a couple of small areas. The estimated thickness is 2.1mm as measured in the metallographic section. It has a dendritic structure (Fig. 1). Sulphide inclusions are seen. There also are voids.

**Composition:**

**AAS:**

| Cu | Sn | Pb | Fe | As | Co | Zn | Ni | Ag | Au | Sb | Bi | total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ( | wt% | | ) | ( | | | ppm | | | | ) | (wt%) |
| 79.32 | 9.78 | 0.13 | 0.19 | nd | nd | 451 | nd | 376 | nd | nd | nd | 89.50 |

**Microanalysis:**

SEM/EDS semi-quantitative analysis was carried out on the least corroded area (600x), the result is shown below:

| Cu | Sn | Fe | Pb | Total |
|---|---|---|---|---|
| 89.3 | 10.1 | 0.2 | 0.1 | 99.7 |

**Microhardness:** 116Hv

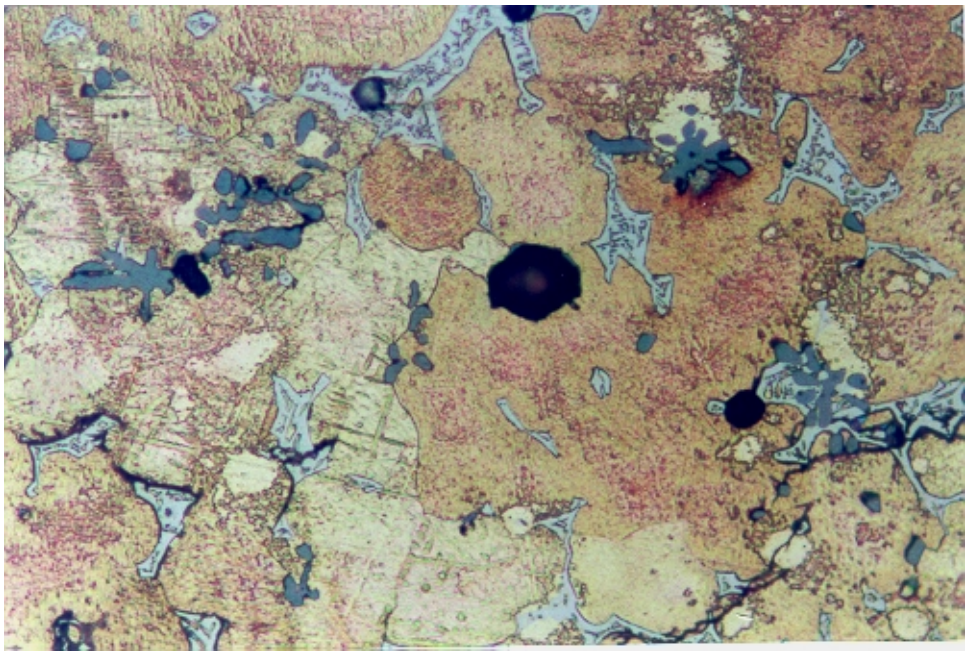


Fig. 1 Dendritic microstructure. Etched in aqueous $FeCl_3$.

BF. Width of the image = 0.2 mm.

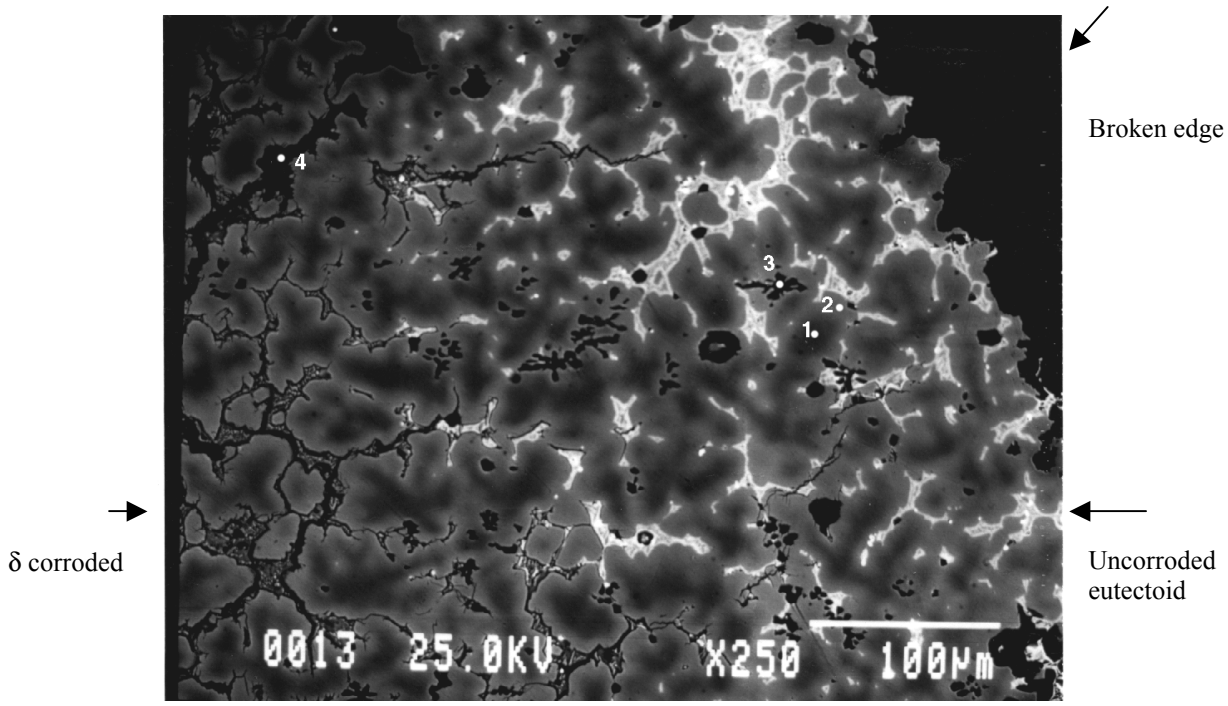



Fig. 2 BEI of metal, showing EPMA points.

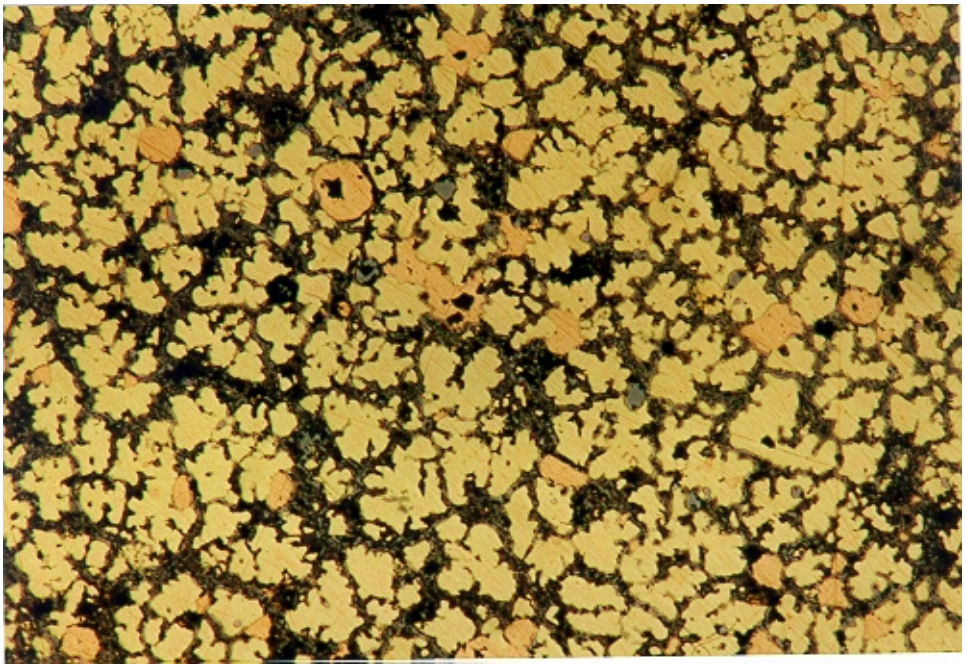


Fig. 3 δ-removal area with redeposited Cu. BF. Width of the image = 1mm.

Fig. 4 Photomicrograph of heavily corroded area with chlorides (likely nantokite based on EPMA data). α islands and particles of redeposited copper are present in the mass of chlorides. BF. Width of the image = 1 mm.

## CORROSION

**XRD results:** not carried out.

### Metallographic observation:

Most of the section is generally corroded, α remains but δ has been attacked by corrosion. Nevertheless, there are several areas on the surface where δ remains (Fig. 2). Redeposited Cu is present in the corroded metal (Fig. 3) or in the corrosion products (Fig. 4). Some of the redeposited Cu has voids in the centre. An area at a corner is heavily corroded with a little isolated α phases and redeposited Cu remaining (Fig. 4). Bronze disease is suspected in this area. Corrosion overburden on both surfaces is thin and mainly comprised of malachite on one surface, and malachite and soil on the other.

### Microanalysis:

EPMA was carried out on metal (Fig. 2), redeposited Cu (Fig. 5) and the heavily corroded area (Fig. 6); the results are as follow:

| Point | Description |
|---|---|
| **1** | α core |
| **2** | Edge of α phase |
| **3** | Sulphide inclusion |
| **4** | Corroded eutectoid |
| **5** | Redeposited Cu |
| **6** | Cuprite |
| **7** | Redeposited Cu |
| **8** | Cuprite |
| **9** | Nantokite |
| **10, 11, 12** | Mixed corrosion products of oxide and chlorides |

| Point | Cu | Fe | Au | Ni | Sn | Pb | Zn | Ag | Hg | As | Sb | Bi | Co | S | Cl | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 89.54 | 0.23 | 0.00 | 0.00 | 8.88 | 0.00 | 0.00 | 0.07 | 0.10 | 0.00 | 0.00 | 0.08 | 0.01 | 0.04 | 0.00 | 98.95 |
| **2** | 69.40 | 0.07 | 0.04 | 0.00 | 31.11 | 0.15 | 0.00 | 0.04 | 0.00 | 0.00 | 0.00 | 0.00 | 0.02 | 0.00 | 0.00 | 100.84 |
| **3** | 72.99 | 1.39 | 0.17 | 0.01 | 9.14 | 0.18 | 0.00 | 0.00 | 0.13 | 0.02 | 0.00 | 0.40 | 0.00 | 2.73 | 0.00 | 87.17 |
| **4** | 64.40 | 0.20 | 0.09 | 0.00 | 22.25 | 0.15 | 0.00 | 0.07 | 0.00 | 0.00 | 0.00 | 0.08 | 0.00 | 0.02 | 0.00 | 87.25 |
| **5** | 97.27 | 0.00 | 0.00 | 0.00 | 0.00 | 0.08 | 0.00 | 0.10 | 0.02 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 97.49 |
| **6** | 84.23 | 0.01 | 0.00 | 0.00 | 0.07 | 0.08 | 0.00 | 0.02 | 0.07 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.06 | 84.55 |
| **7** | 97.48 | 0.01 | 0.00 | 0.00 | 0.00 | 0.09 | 0.00 | 0.02 | 0.08 | 0.00 | 0.00 | 0.13 | 0.01 | 0.00 | 0.00 | 97.82 |
| **8** | 87.02 | 0.00 | 0.00 | 0.00 | 0.04 | 0.00 | 0.09 | 0.10 | 0.00 | 0.23 | 0.00 | 0.16 | 0.00 | 0.05 | 0.00 | 87.69 |
| **9** | 61.80 | 0.01 | 0.06 | 0.00 | 0.03 | 0.00 | 0.03 | 0.05 | 0.02 | 0.04 | 0.00 | 0.00 | 0.00 | 0.01 | 34.91 | 96.95 |
| **10** | 15.12 | 0.20 | 0.00 | 0.00 | 6.63 | 0.00 | 0.24 | 0.01 | 0.00 | 0.00 | 0.00 | 0.05 | 0.01 | 0.09 | 3.25 | 25.59 |
| **11** | 58.60 | 0.22 | 0.00 | 0.00 | 17.04 | 0.16 | 0.00 | 0.02 | 0.00 | 0.24 | 0.00 | 0.06 | 0.00 | 0.13 | 5.21 | 81.65 |
| **12** | 84.90 | 0.30 | 0.05 | 0.00 | 6.43 | 0.13 | 0.00 | 0.14 | 0.00 | 0.12 | 0.00 | 0.00 | 0.01 | 0.12 | 2.99 | 95.20 |

EPMA data shows that the void in the center of redeposited Cu is filled with cuprite (point 8), The ratio of Cu/Cl indicates that nantokite is present in the heavily corroded area (point 9).

**SUMMARY**

It is a binary alloy of Cu-Sn with a dendritic structure. The best estimated composition determined by SEM/EDS is 89% Cu and 10% Sn. Redeposited Cu with voids is present. Chloride attack is confirmed by EPMA.

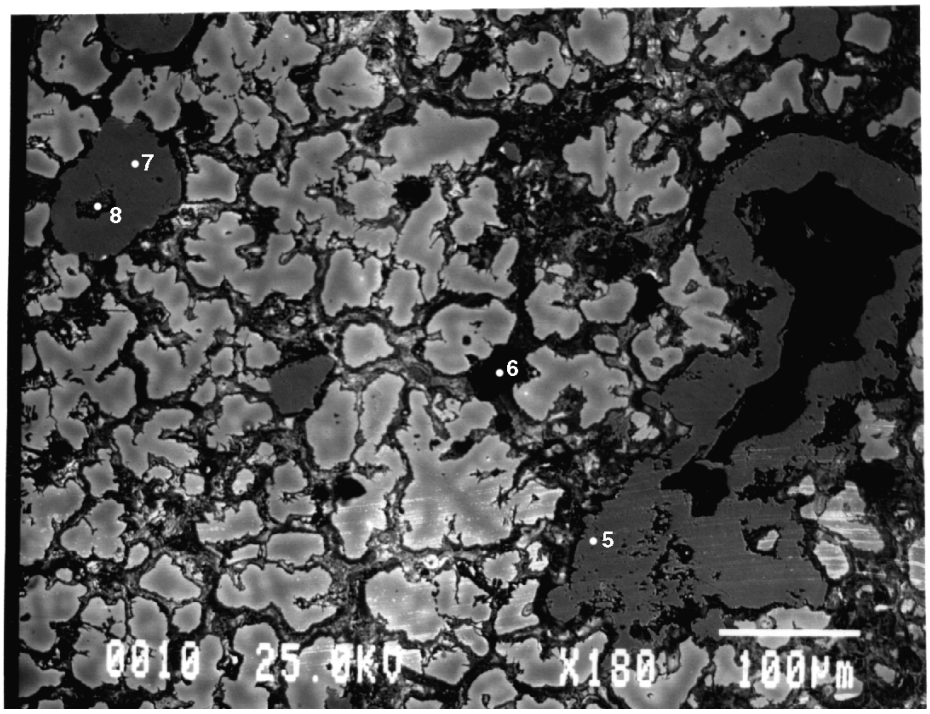



Fig. 5 BEI of redeposited Cu, showing EPMA points.

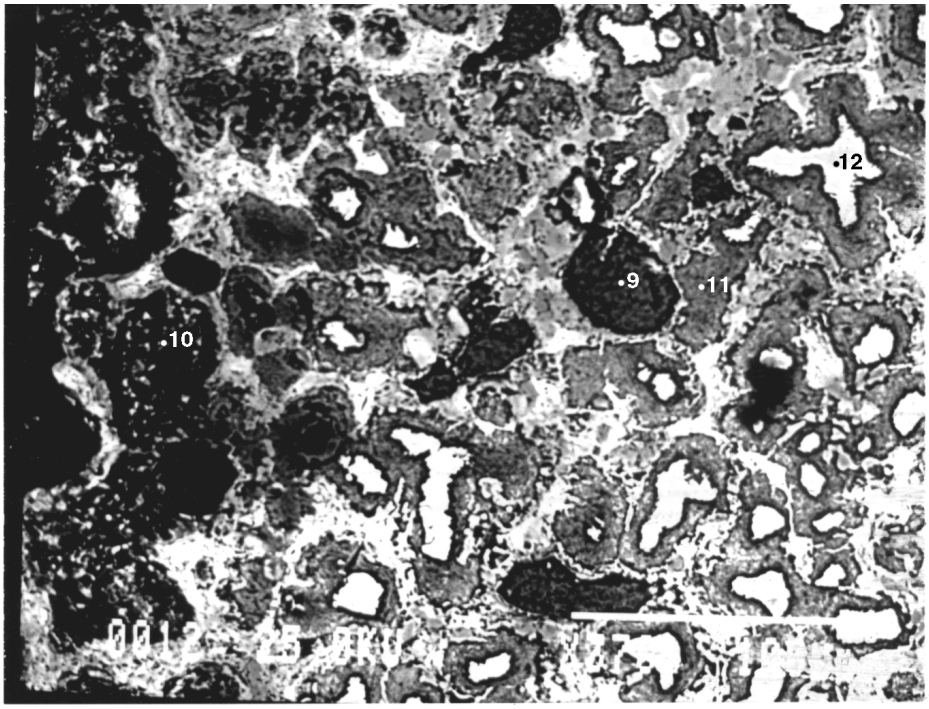



Fig. 6 BEI of the heavily corroded area, showing EPMA points.

## GENERAL

**Object Number:** M64:148
**Excavation Date:** 1994
**Origin:** Tianma-Qucun site

**Object:** vessel/*ding*
**Date:** Late Western Zhou
**Fragment Weight:** 0.7 g
**Fragment size:** 11x9x1.8 mm

**General description:**

This fragment has deep corrosion. It is easily broken. Corrosion index is 4. There is a thin corrosion overburden on one surface but a thick one on the other surface. One surface is covered with green, red and white corrosion products; the other surface is covered with green, dark green and white corrosion products and soil. No decoration is apparent.

## TECHNICAL STUDIES OF METAL

**Metallographic structure:**

The flat surfaces on both sides indicate that the fragment was from a flat part of the object such as the base. The original surface can be seen on one side (left in Fig. 1) while it is disrupted on the other side (right in Fig. 1). The estimated thickness is 1.8 mm as measured in the metallographic section. It is a cast dendritic structure (Fig. 2). Pb droplets are seen.

**Composition:**

**AAS:** too corroded for analysis

**Microanalysis:**

SEM/EDS semi-quantitative analysis was carried out on the least corroded area (500x), the result shows that it is a ternary alloy of Cu-Sn-Pb. The lower total is due to corrosion.

| Cu | Sn | Pb | Total |
|---|---|---|---|
| 69.2 | 7.2 | 10.0 | 86.4 |

**Microhardness:** too corroded for measuring

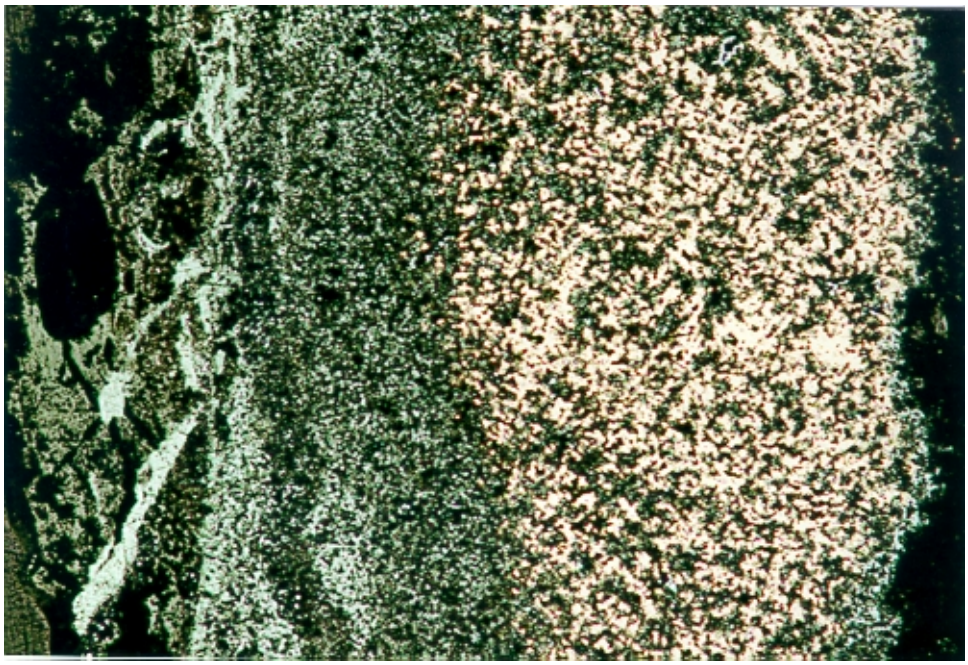


Fig. 1 Metallographic section, showing the original surface on the left side and corrosion penetrating all the way into the metal. BF. Width of the image = 2 mm.

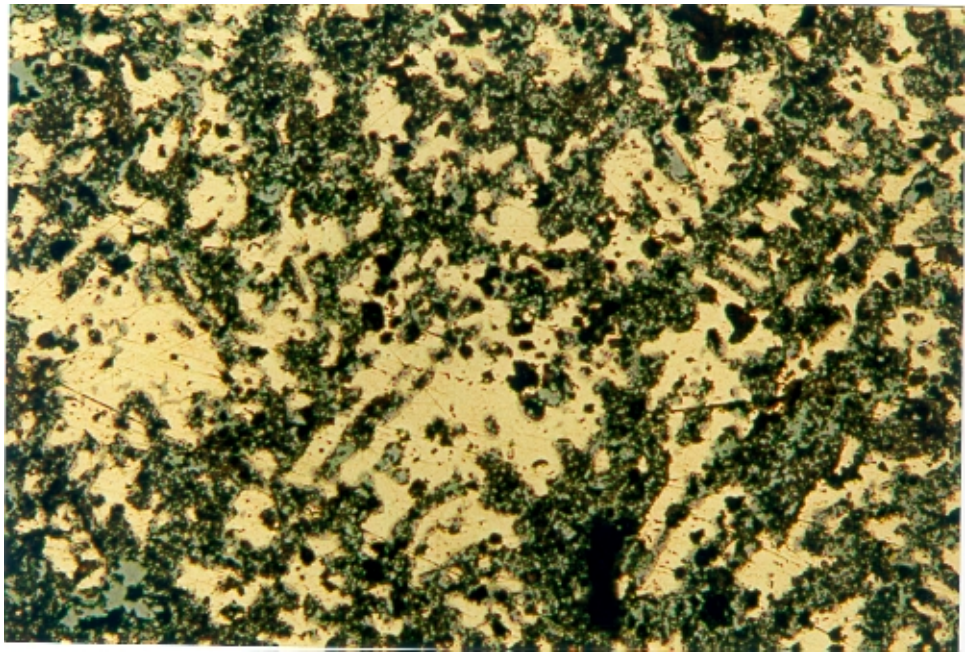


Fig. 2 Photomicrograph of corroded metal showing islands of uncorroded α phase and Pb droplets (the darker spots). BF. Width of the image = 0.5 mm.

## CORROSION

### XRD results:

White corrosion product on the surface: cerussite, quartz.

### Metallographic observation:

Corrosion goes through all the way to the metal, on the side with thicker corrosion overburden, most of the original dimension of the metal is totally corroded without any remnant metallic phase (Fig. 1). No δ phase is seen at all.

Based on their characteristic colours in the metallographic section and EPMA data (see below) corrosion products on the surface are identified to be mixture of cuprite and cassiterite, copper sulphide and cassiterite, cuprite, cerussite and malachite in sequence from the original surface outwards.

### Microanalysis:

SEM/EDS colour maps have been done on the corrosion on the surface (Fig. 3), the result shows the presence of Pb (75.5% Pb at Pb-rich area) and Si in the corrosion. This is confirmed by XRD. The presence of a cerussite layer on the surface suggests that the original content of Pb could be higher than 10% (measured on corroded metal). Microprobe analysis was carried out on the corroded metal (Fig. 4) and corrosion (Fig. 5); the results are as follows:

| Point | Description |
|---|---|
| **1** | α phase |
| **2** | Pb, beam probably shifted to corrosion |
| **3, 4, 5** | Corrosion inside the metal |
| **6** | Cerussite |
| **7** | Copper sulphide/sulphate |
| **8** | Cuprite |
| **9** | Sulphides |

| point | Cu | Fe | Au | Ni | Sn | Pb | Zn | Ag | Hg | As | Sb | Bi | Co | S | Cl | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 89.02 | 0.04 | 0.00 | 0.01 | 3.74 | 0.15 | 0.00 | 0.10 | 0.01 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 93.08 |
| **2** | 39.03 | 0.06 | 0.01 | 0.04 | 0.96 | 18.10 | 0.00 | 0.05 | 0.04 | 0.07 | 0.00 | 0.00 | 0.02 | 0.06 | 0.02 | 58.46 |
| **3** | 21.92 | 0.09 | 0.00 | 0.02 | 6.08 | 26.08 | 0.00 | 0.24 | 0.00 | 0.24 | 0.00 | 0.01 | 0.02 | 0.05 | 0.72 | 55.48 |
| **4** | 67.02 | 0.14 | 0.00 | 0.00 | 7.28 | 5.61 | 0.00 | 0.07 | 0.00 | 0.07 | 0.00 | 0.50 | 0.01 | 0.55 | 0.65 | 81.89 |
| **5** | 71.45 | 0.14 | 0.00 | 0.00 | 4.99 | 2.42 | 0.00 | 1.69 | 0.00 | 0.00 | 0.00 | 0.27 | 0.00 | 0.00 | 0.38 | 81.34 |
| **6** | 0.16 | 0.03 | 0.05 | 0.00 | 0.02 | 84.31 | 0.03 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.20 | 84.80 |
| **7** | 67.87 | 0.02 | 0.00 | 0.00 | 0.04 | 3.74 | 0.00 | 0.08 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 18.55 | 0.50 | 90.77 |
| **8** | 79.65 | 0.00 | 0.06 | 0.00 | 0.01 | 1.00 | 0.00 | 0.00 | 0.00 | 0.09 | 0.00 | 0.00 | 0.00 | 0.00 | 0.06 | 80.88 |
| **9** | 65.16 | 0.07 | 0.00 | 0.02 | 8.33 | 8.46 | 0.00 | 1.02 | 0.00 | 0.00 | 0.00 | 0.25 | 0.00 | 16.85 | 0.52 | 100.67 |

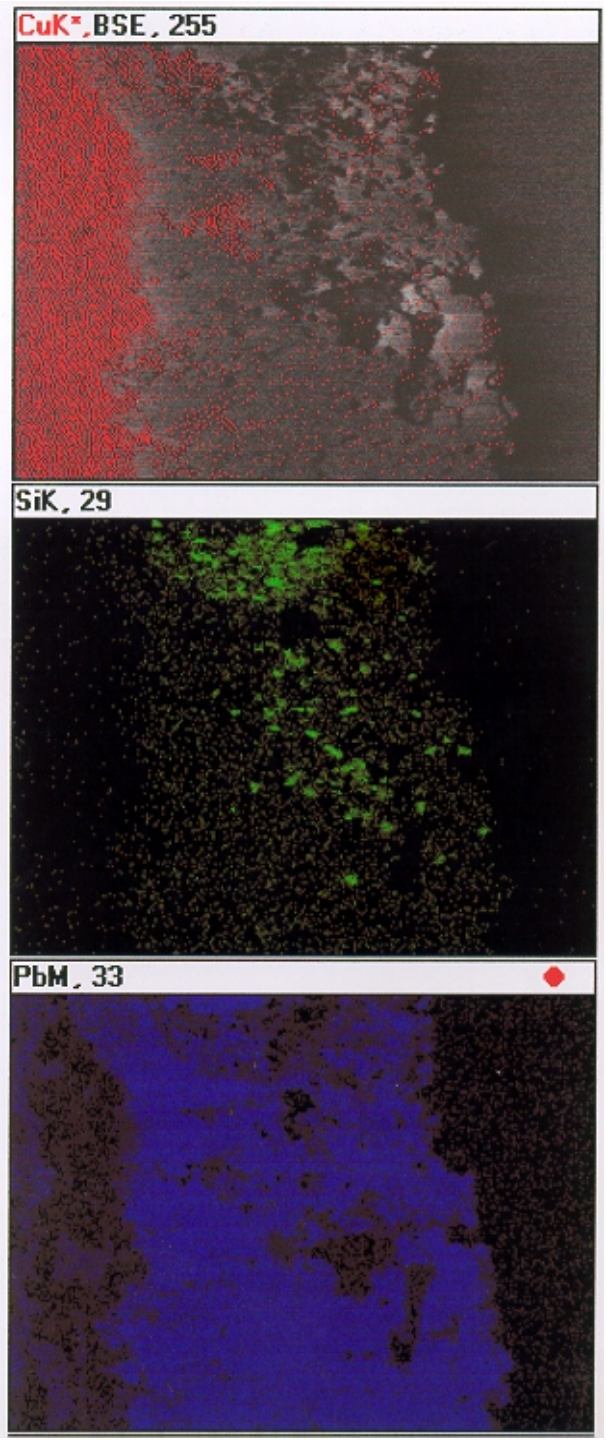



Fig. 3 SEM/EDS colour map on corrosion on a surface. The metal is on the left. 100x.

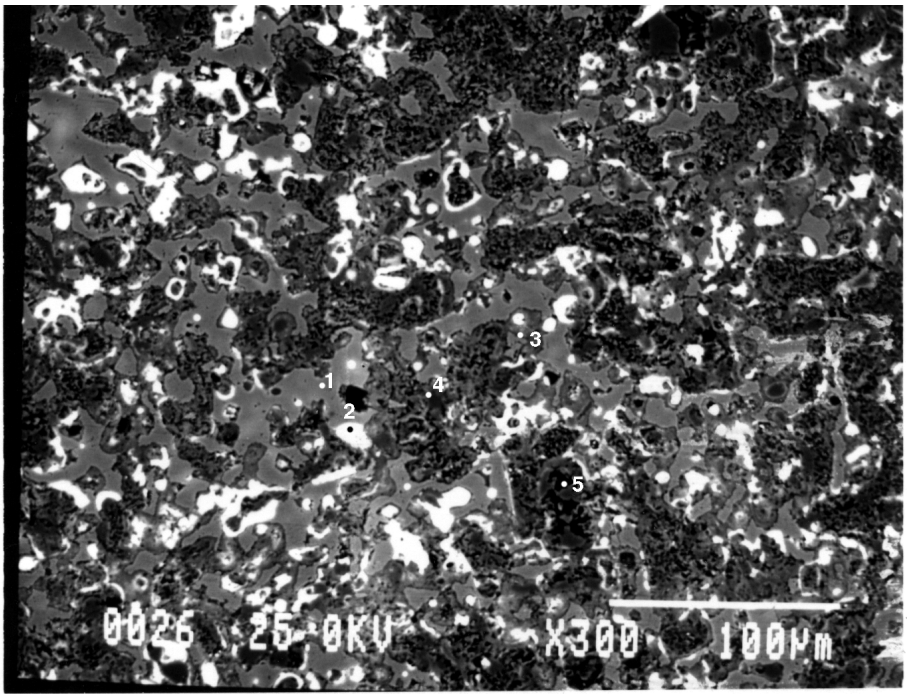



Fig. 4 BEI of corroded metal, showing EPMA points.

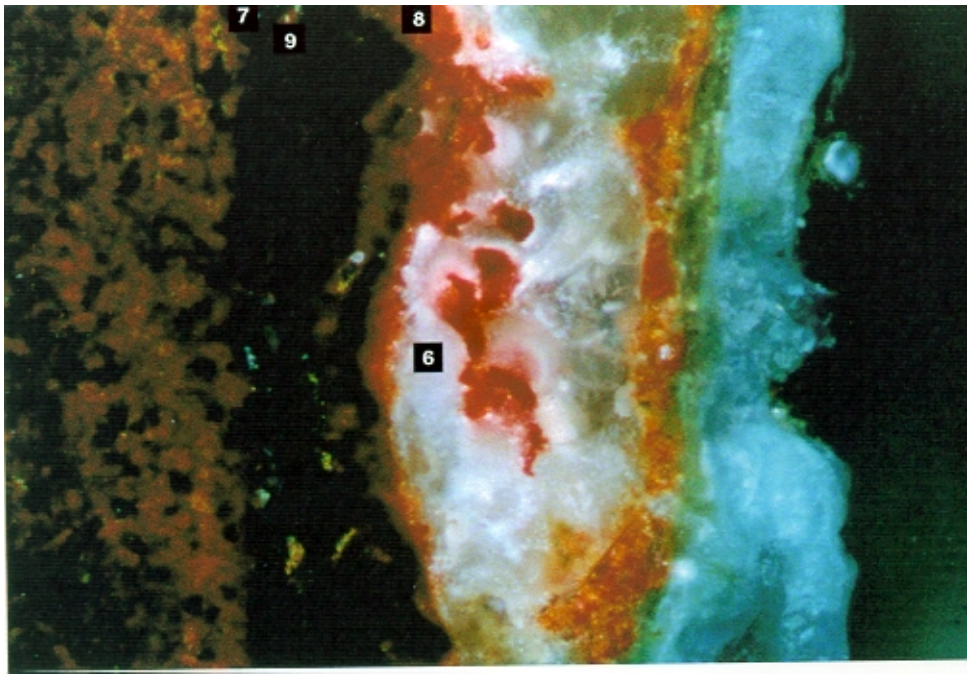



Fig. 5 Photomicrograph of corrosion on the surface. C/P. Width of the image = 1 mm.

## SUMMARY

It is a ternary alloy of Cu-Sn-Pb with a dendritic structure. It is corroded badly with Pb having been converted to cerussite. The bulk composition determined by SEM/EDS is 69% Cu, 7% Sn and 10% Pb. The original contents of Pb and Cu could be higher than these figures judged from the corrosion products on the surface.

## GENERAL

**Object Number:** M93:fish1
**Excavation Date:** 1994
**Origin:** Tianma-Qucun site

**Object:** ornament/fish tail
**Date:** Early Spring and Autumn period
**Fragment Weight:** 4.5 g
**Fragment size:** 36x15x1.5 mm

**General description:**

This fragment has one side (top of Fig. 1) broken. Corrosion index is 2. There is nearly no corrosion overburden. Some compact waxy white material, green corrosion and soil are only seen in some areas of the fragment. There are negative decoration lines on a surface (Fig. 1)

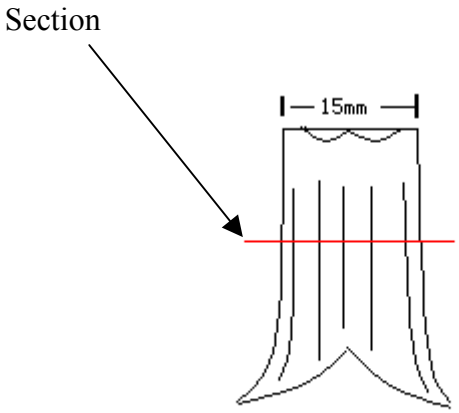



Fig. 1 Surface decoration patterns

## TECHNICAL STUDIES OF METAL

**Metallographic structure:**

A section cut along the centre of fragment (Fig. 1) was taken for metallographic observation. The overall view of the metallographic section is shown in Fig. 2. The estimated original thickness is 1.5 mm as measured in the metallographic section. The metallographic structure under the decoration confirms it was cast. Metallography shows this is a leaded bronze, with Pb droplets of different shapes and sizes (Fig. 3). The biggest Pb droplet is about 196x123 μm. The distribution of Sn is not even in the uncorroded metal, being more in some areas than other ones. The

presence of eutectiods and big Pb droplets suggests it has been cast with a slow cooling rate.

## Composition:

**AAS:**

| **Cu** | **Sn** | **Pb** | **Fe** | **As** | **Co** | **Zn** | **Ni** | **Ag** | **Au** | **Sb** | **Bi** | **total** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ( | wt% | | ) | ( | | | ppm | | | | ) | (wt%) |
| 72.32 | 10.88 | 11.07 | 0.069 | nd | nd | 424 | 112 | 2009 | nd | nd | 1786 | 94.77 |

**Microanalysis:**

See corrosion section

**Microhardness:** 95Hv

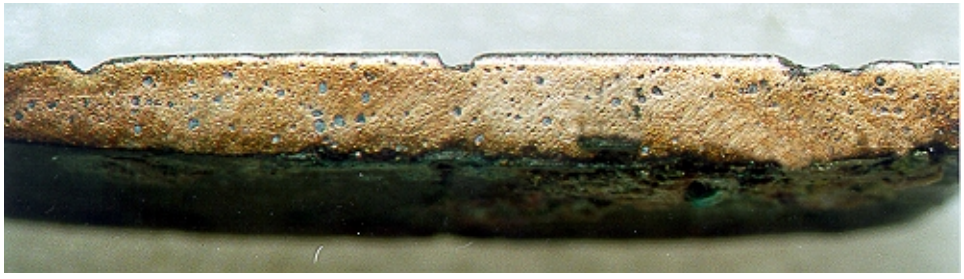


Fig. 2 Metallographic section, showing surface decoration cavities. The black painting on the polished surface is carbon coating. BF. Thickness at the middle of the section = 1.5 mm.

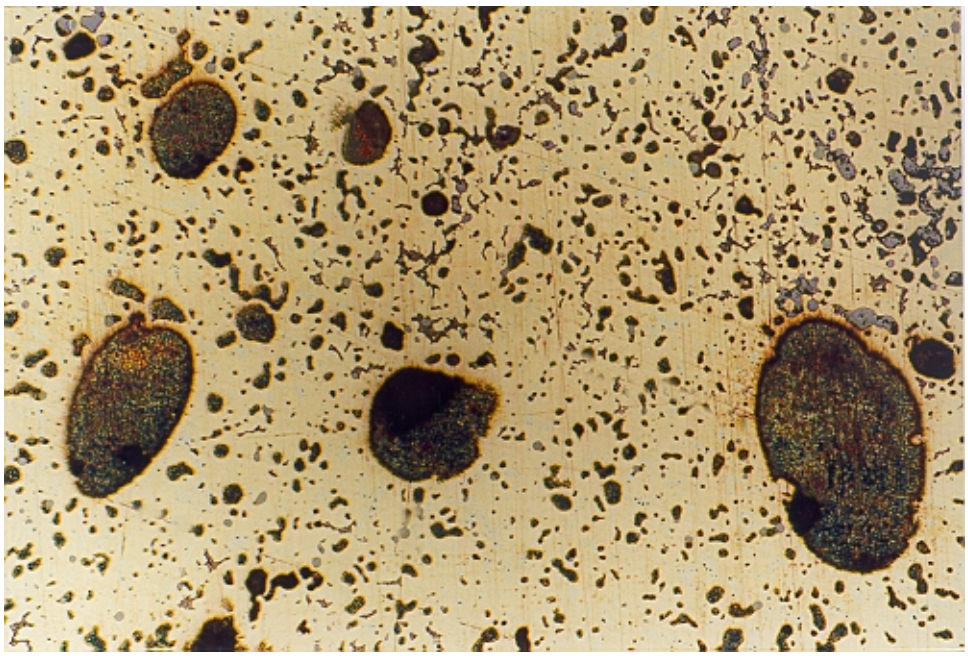


Fig. 3 Microstructure with big Pb globules. BF. Width of the image = 0.7 mm.

## CORROSION

### XRD results:

Surface sample: cerussite, malachite, calcite.

### Metallographic observation:

Most of the metal is uncorroded. Some lead globules are partially corroded (Fig. 3). The darker area of these lead globules seems to be chloride. There is a layer of corrosion on the surface without decoration. Two types of corrosion: α-removal and δ-removal, are present. Redeposited Cu can be seen on the surface (Fig. 4). Slip lines on the surface are probably the result of crystallographic corrosion.

### Microanalysis:

The corrosion layer on the undecorated surface is evident in a secondary electron image (Fig. 5). SEM/EDS confirms it is lead compound, so it must be cerussite based XRD. EPMA spot analyses were carried out on the metal matrix and lead globules, which confirm that the corroded part of the lead globules contained Cl. This is also seen in sample M93:fish2 and M6231:69(1). These chloride ions must have gone into the metal from surface but without access to oxygen and water. So bronze disease was not able to develop.

| Point | Cu | Fe | Sn | Pb | As | S | Cl | Total | Description |
|---|---|---|---|---|---|---|---|---|---|
| **1** | 88.01 | 0.07 | 9.89 | 1.67 | 0.00 | 0.08 | 0.02 | 99.74 | Matrix |
| **2** | 86.02 | 0.05 | 11.70 | 0.39 | 0.00 | 0.01 | 0.00 | 98.17 | Matrix |
| **3** | 33.47 | 0.07 | 4.19 | 47.31 | 0.00 | 0.00 | 10.79 | 95.83 | Partially corroded lead |
| **4** | 38.16 | 0.09 | 4.32 | 44.11 | 0.00 | 0.00 | 10.28 | 96.96 | Partially corroded lead |
| **5** | 1.28 | 0.36 | 1.19 | 96.07 | 0.00 | 0.62 | 0.00 | 99.52 | Metallic lead |
| **6** | 2.49 | 0.33 | 1.37 | 93.53 | 0.00 | 0.49 | 0.00 | 98.21 | Metallic lead |
| **7** | 65.39 | 0.23 | 23.93 | 4.49 | 0.00 | 0.14 | 0.25 | 94.43 | Corroded area under surface |

## SUMMARY

It is a ternary alloy of Cu-Sn-Pb, with relatively high content of Ag and Bi. The bulk composition determined by AAS is 72.3% Cu, 10.9% Sn and 11.1% Pb, which is probably less copper and lead than in the original alloy, since some Pb (probably

with Cu) globules have partially corroded and converted to chlorides. Surface decoration patterns were cast. Redeposited Cu is present on the surface.

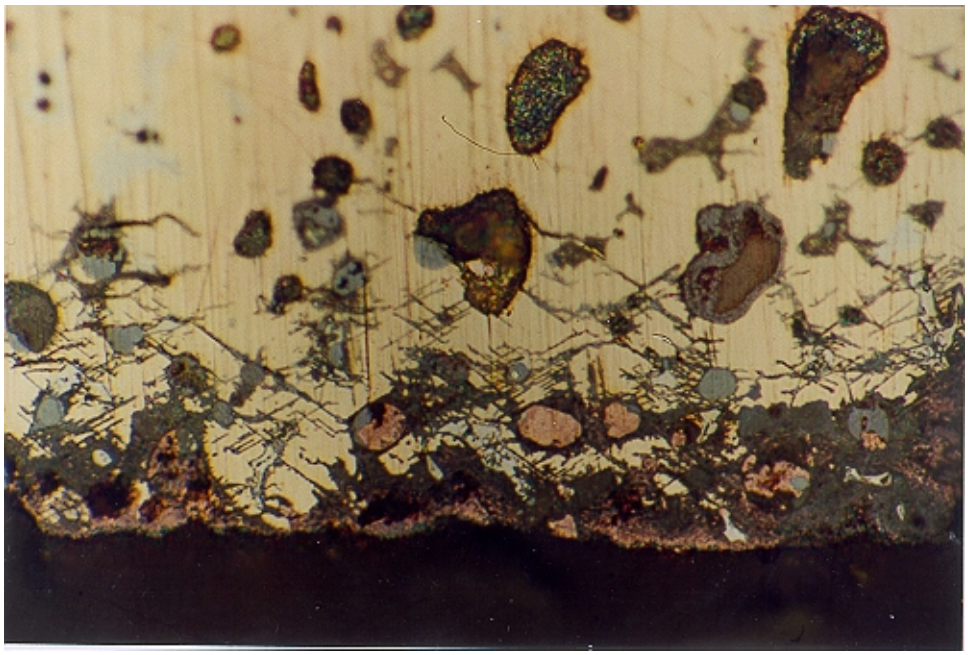


Fig. 4 Photomicrograph of a surface, showing redeposited Cu. BF. Width of the image = 0.15 mm.

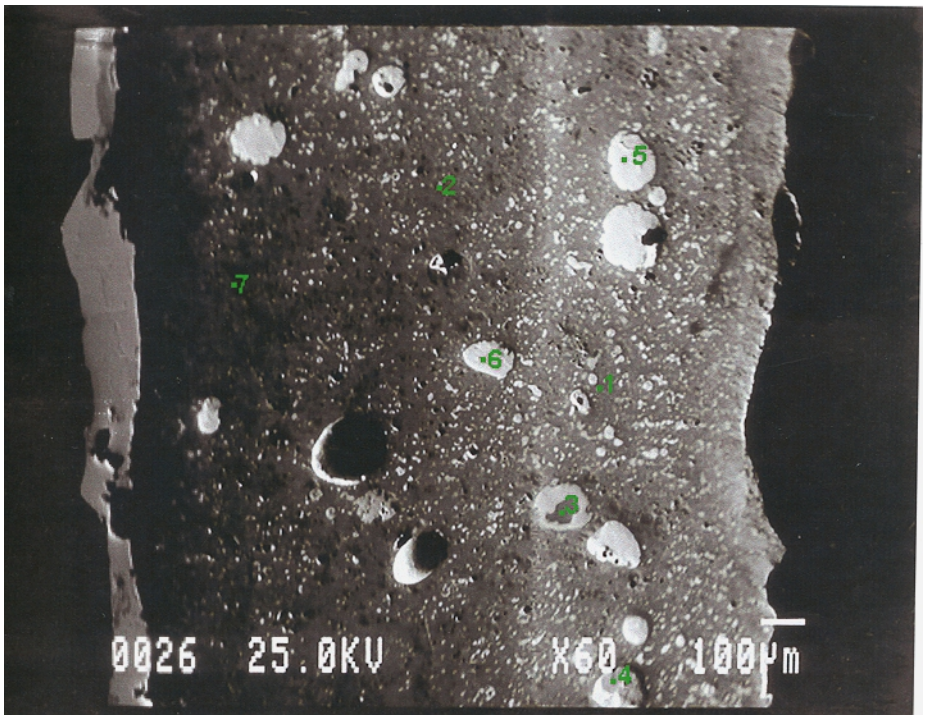



Fig. 5 BEI of the metallographic section, showing cerussite layer on a surface and EPMA ponits.

## GENERAL

**Object Number:** M93:fish2

**Object:** ornament/fish tail

**Excavation Date:** 1994

**Date:** Early Spring and Autumn period

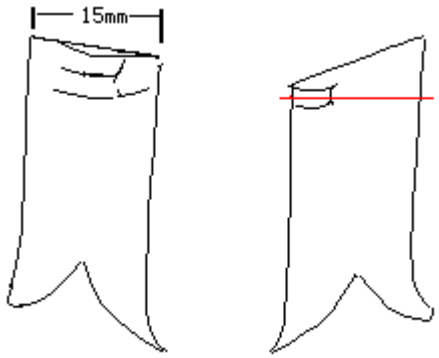
**Origin:** Tianma-Qucun site

**Fragment Weight:** 4.7g

**Fragment size:** 33x15x1.5 mm

**General description:**

This fragment is similar to M93:fish1, with nearly no corrosion overburden. Corrosion index is 2. Negative decoration lines are shown up on a surface after mechanical cleaning (Fig. 1)




Back Front

Fig. 1 surface decoration patterns

## TECHNICAL STUDIES OF METAL

**Metallographic structure:**

A section cut across the decoration patterns of the fragment (Fig. 1) was taken for metallographic observation. The estimated original thickness is 1.4 mm as measured in the metallographic section. Metallography shows this is a leaded bronze, Pb is present as both globules and elongated droplets, with uneven sizes of up to 10 micros in diameter (Fig. 2). The small size of lead suggests a fast cooling rate of this piece. The presence of eutectiod shows that it is a cast structure.

**Composition:**

**AAS:**

| **Cu** | **Sn** | **Pb** | **Fe** | **As** | **Co** | **Zn** | **Ni** | **Ag** | **Au** | **Sb** | **Bi** | **total** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ( | wt% | | ) | ( | | | ppm | | | | ) | (wt%) |
| 65.23 | 10.95 | 8.95 | 1.541 | nd | nd | 282 | 150 | 752 | nd | nd | nd | 86.78 |

**Microanalysis:**

Backscattered electron image of the section (Fig. 3) shows that Pb precipitates toward the middle from the surfaces, this indicates that this piece was cast in a 2 pieces-mould with one side down.

**Microhardness:** 98Hv

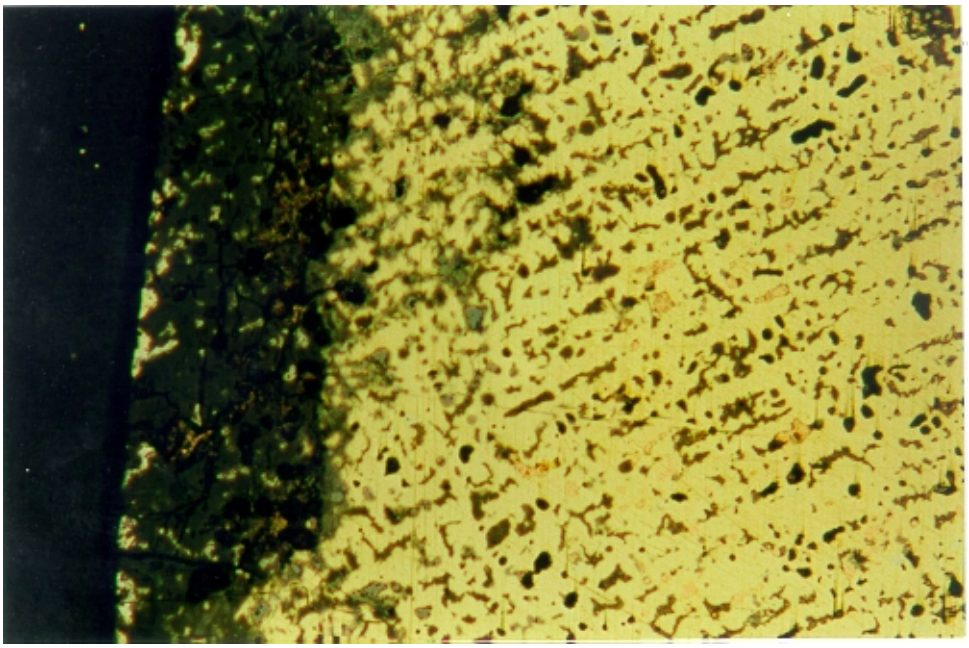


Fig. 2 Microstructure of the metal, showing disrupted surface. BF. Width of the image = 0.5 mm.

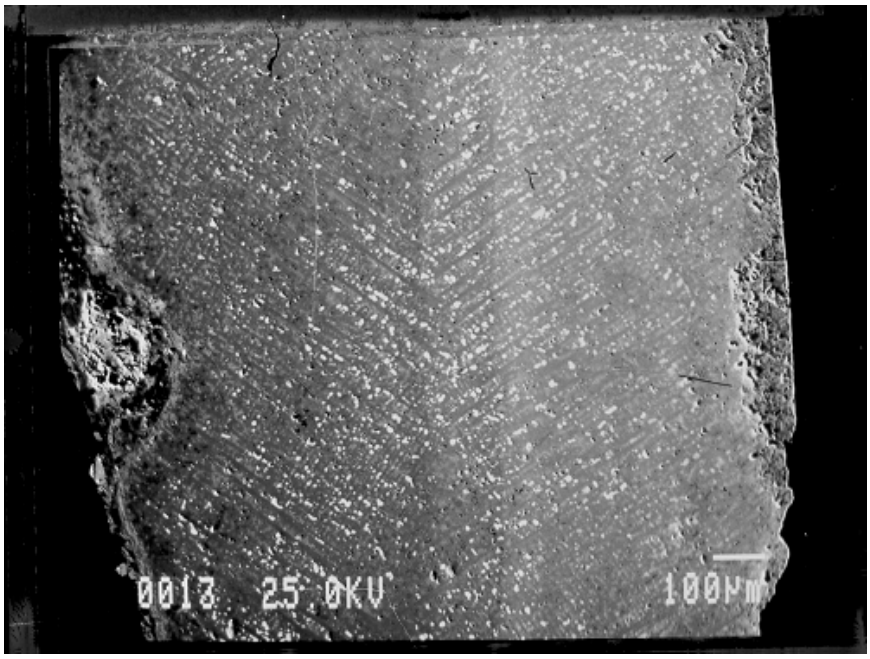



Fig. 3 BEI of microstructure, showing segregation direction of Pb.

## CORROSION

**XRD results:** not carried out.

**Metallographic observation:**

The original surfaces are preserved well in most areas but disrupted in some (Fig. 2). The original dimensions are still retained (Fig. 2). It seems that one surface has been disrupted by chlorides. Redeposited Cu is seen in the metal (Fig. 4) and in the corrosion overburden as well.

**Microanalysis:**

EPMA point analyses were carried out on metallic lead (point 1), α phase (point 2, 3), and a corrosion pit in a decoration concavity on the surface (point 4-14). The results show $Cl^-$ is present in the corrosion pit, which is probably copper or lead chloride.

| Point | Cu | Fe | Sn | Pb | As | S | Cl | Sb | Bi | Ag | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 5.41 | 0.12 | 0.01 | 88.08 | 0.00 | 0.00 | 0.18 | 0.03 | 0.00 | 0.00 | 93.83 |
| **2** | 86.44 | 0.35 | 10.24 | 0.41 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.04 | 97.48 |
| **3** | 76.06 | 0.27 | 14.06 | 2.16 | 0.00 | 0.01 | 0.00 | 0.00 | 0.08 | 0.11 | 92.75 |
| **4** | 46.85 | 0.04 | 0.00 | 13.63 | 0.00 | 0.00 | 0.84 | 0.02 | 0.00 | 0.00 | 61.38 |
| **5** | 38.26 | 0.06 | 0.07 | 41.55 | 0.00 | 0.00 | 13.28 | 0.00 | 0.00 | 0.00 | 93.22 |
| **6** | 43.73 | 0.16 | 0.01 | 30.78 | 2.99 | 0.00 | 5.79 | 0.00 | 0.03 | 0.00 | 83.49 |
| **7** | 72.34 | 0.01 | 0.00 | 0.23 | 0.00 | 0.01 | 0.05 | 0.00 | 0.00 | 0.03 | 72.66 |
| **8** | 20.35 | 0.12 | 0.01 | 53.90 | 0.00 | 0.00 | 11.56 | 0.00 | 0.00 | 0.00 | 85.92 |
| **9** | 5.18 | 0.22 | 0.10 | 64.39 | 0.00 | 0.00 | 7.44 | 0.06 | 0.00 | 0.00 | 77.39 |
| **10** | 30.19 | 0.06 | 0.04 | 49.85 | 0.00 | 0.00 | 12.00 | 0.05 | 0.00 | 0.00 | 92.18 |
| **11** | 56.90 | 0.03 | 0.02 | 18.36 | 0.00 | 0.00 | 5.10 | 0.03 | 0.00 | 0.03 | 80.46 |
| **12** | 41.16 | 3.17 | 0.27 | 22.51 | 0.00 | 1.16 | 5.69 | 0.00 | 0.00 | 0.00 | 73.96 |
| **13** | 14.09 | 0.91 | 17.08 | 25.57 | 0.00 | 0.00 | 5.47 | 0.00 | 0.00 | 0.00 | 63.12 |
| **14** | 44.50 | 0.85 | 13.11 | 16.24 | 0.00 | 0.00 | 4.47 | 0.00 | 0.00 | 0.05 | 79.21 |

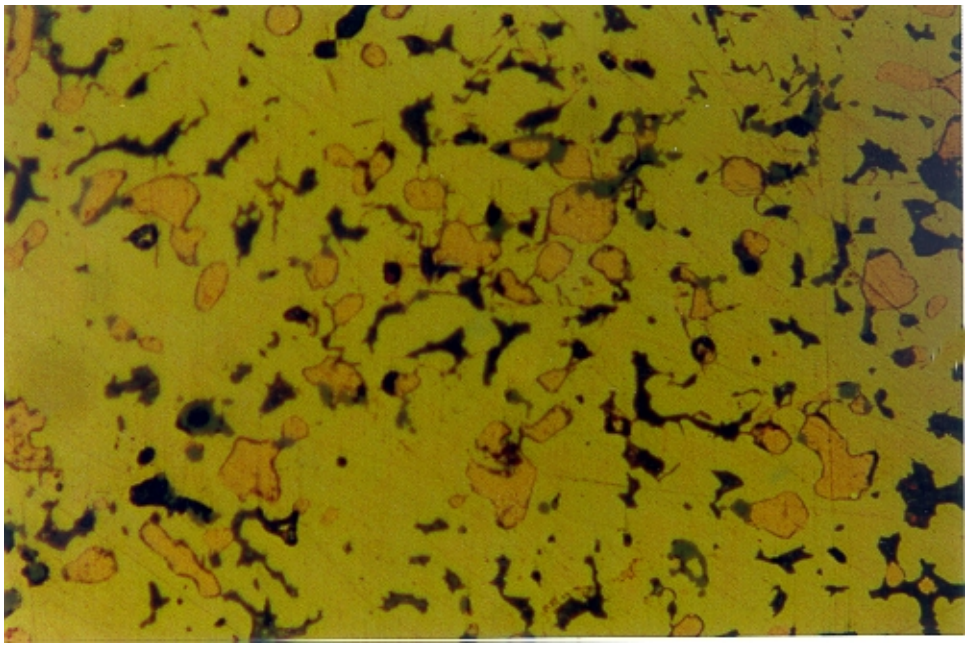


Fig. 4 Photomicrograph of redeposited Cu in metal. BF. Width of the image = 0.2 mm.

## SUMMARY

It is a ternary alloy of Cu-Sn-Pb with a cast dendritic structure. The bulk composition determined by AAS is 65.2% Cu, 11.0% Sn, 9.0% Pb and 1.5% Fe. The content of Cu and Pb is expected to be higher for the original alloy as discussed for sample M93: fish1. Some Pb globules have corroded. Lead or/and copper chlorides are present in the corrosion on the surface. Redeposited Cu is present in the metal.

## GENERAL

**Object Number:** M6231:1
**Object:** vessel/*yan*
**Excavation Date:** 1984
**Date:** Early Western Zhou
**Origin:** Tianma-Qucun site
**Fragment Weight:** 2.2 g
**Fragment size:** 20x4x2 mm

**General description:**

This fragment is from the sidewall of the top part of the vessel (Fig. 1). Corrosion index is 4. There is a thick corrosion overburden on the surface, including light green, green, red and black corrosion products and soil. No decoration is apparent (Fig. 2)

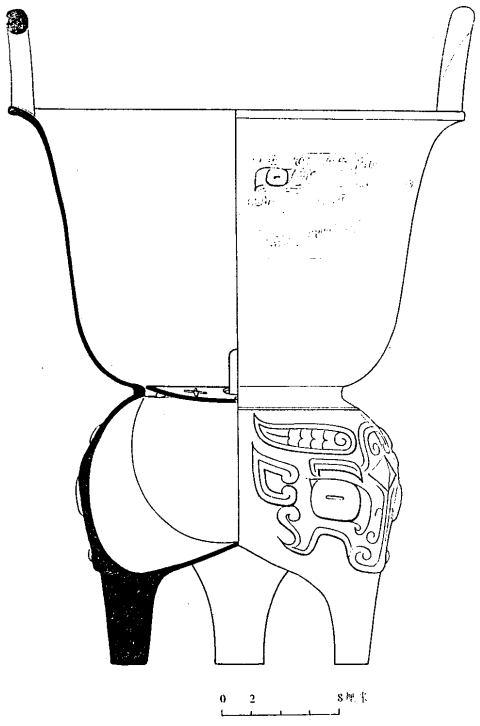


Fig.1 The object (the scale bar is 8 cm)

## TECHNICAL STUDIES OF METAL

**Metallographic structure:**

A section cut through the full width of the fragment was taken for metallographic observation. The original surfaces can still be seen although the metal is deeply corroded (Fig. 3). The estimated thickness is 2 mm as measured in the metallographic section. It has an equi-axed structure with few δ phases being preserved (Fig. 4).

## Composition:

**AAS:** too corroded for analysis.

**Microanalysis:**

SEM/EDS semi-quantitative analysis was carried out on the least corroded area (300x), the result is:

| Fe | Cu | Sn | Pb | Total |
|---|---|---|---|---|
| 0.7 | 49.6 | 11.4 | 9.2 | 70.9 |

EPMA linescan across the metal was carried out, the result is shown in Fig. 5. Fig. 5 shows that Sn is richer in the corroded area than that in the uncorroded area. Sulphur is also richer in the corroded areas than the uncorroded areas. This is due to preferential corrosion of the grain boundaries where sulphide inclusions are usually present. Arsenic was detected in the corroded area but not in the uncorroded metal. Fe shows a correlation with Sn. Lead concentration is also higher in the corroded areas. Therefore, lead content for the bulk metal is expected to be higher than the figure detected by SEM/EDS.

**Microhardness:** 152Hv.

Fig. 2 General view of the fragment.

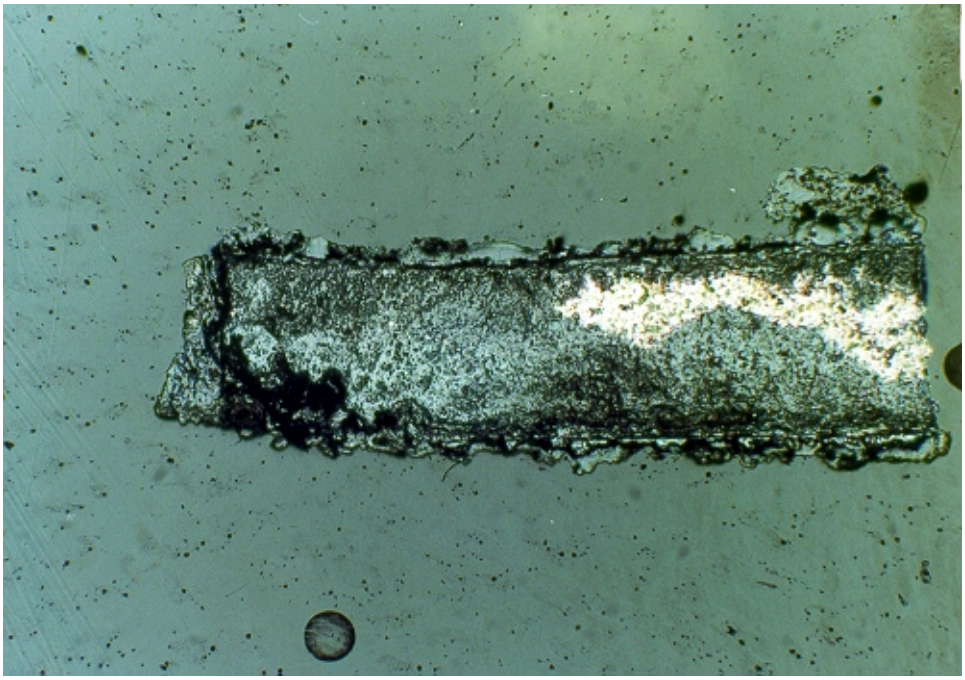


Fig. 3 The metallographic section.
BF. The thickness of the original metal is 2 mm.

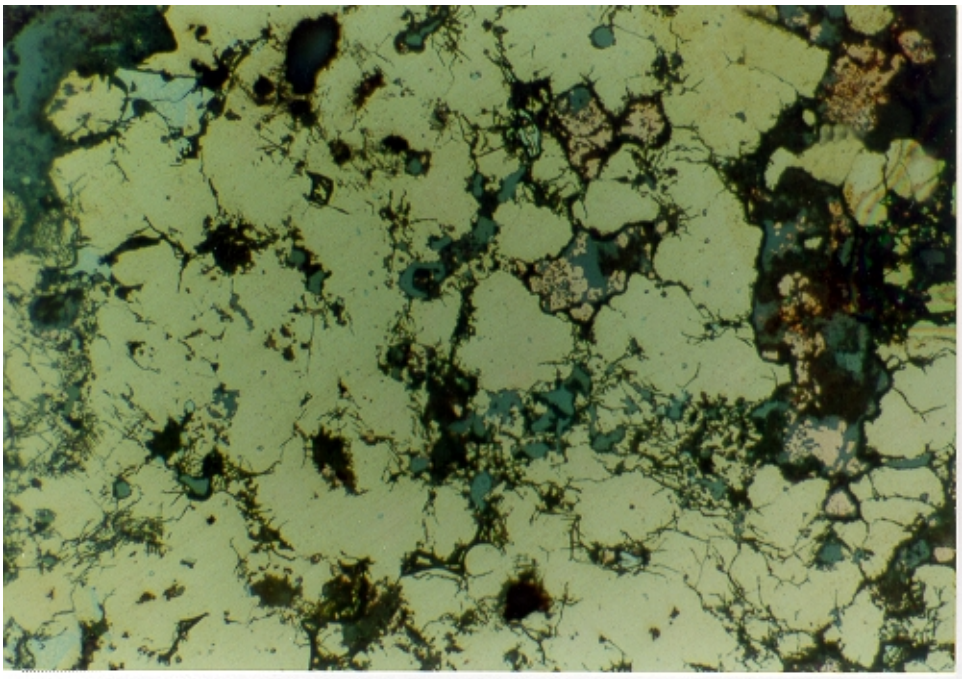
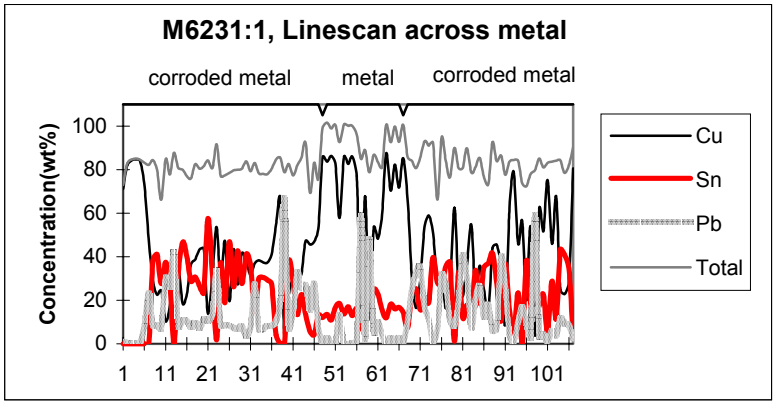
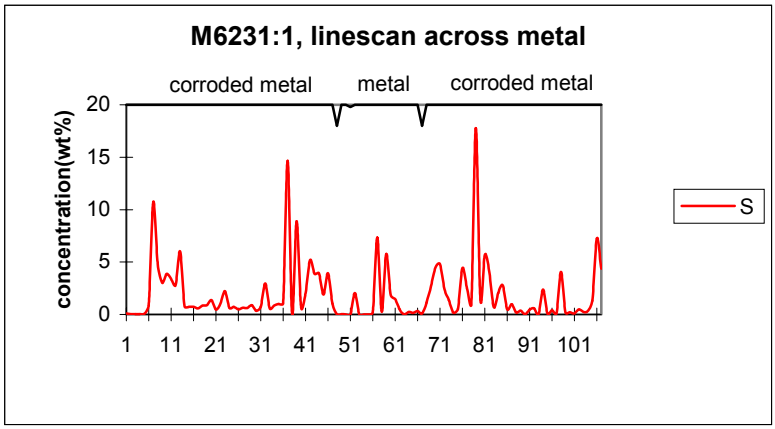
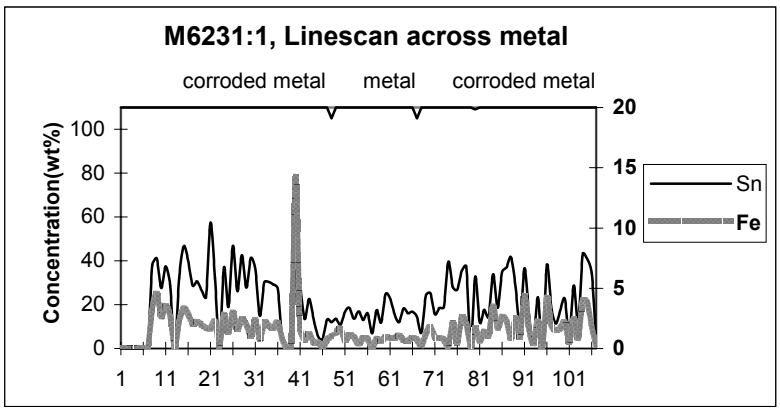


Fig. 4 Equi-axed microstructure, showing redeposited Cu in corrosion.
BF. Width of the image = 0.28 mm.



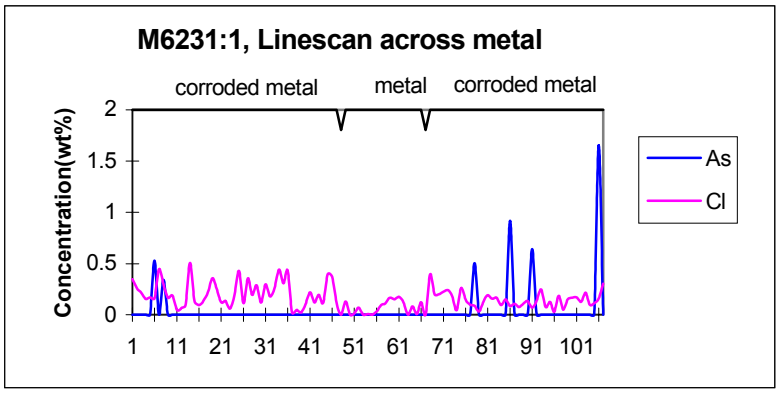




Fig. 5 EPMA linecan across the metal

## CORROSION

### XRD results:

Surface sample: cuprite, cerussite, malachite, quartz.

### Metallographic observation:

The whole piece is corroded with a small area of metal remaining (Fig. 3). Corrosion follows grain boundaries. Redeposited Cu is seen in cuprite (Fig. 4). There is a black layer on one surface (Fig. 6). Corrosion overburden is up to 0.9 mm thick. It is a layered structure, comprised of a black layer, cuprite with sulphide, lead carbonate, and malachite with azurite in sequence from the metal outwards (Fig. 7).

### Microanalysis:

EPMA was carried out on metal (Fig. 8) and the corrosion layer (Fig. 9), the results are shown below:

| Point | Cu | Fe | Sn | Pb | As | S | Cl | Total | Description |
|---|---|---|---|---|---|---|---|---|---|
| **1** | 3.38 | 0.08 | 0.05 | 96.09 | 0.00 | 0.00 | 0.36 | 99.96 | Lead droplet |
| **2** | 41.42 | 0.08 | 0.12 | 39.76 | 0.00 | 1.25 | 2.41 | 85.04 | α phase |
| **3** | 37.33 | 0.44 | 8.10 | 31.87 | 0.00 | 8.28 | 0.28 | 86.30 | Corrosion on boundary |
| **4** | 76.59 | 0.38 | 15.43 | 1.33 | 0.00 | 0.47 | 0.09 | 94.23 | A lighter spot on boundary |
| **5** | 23.04 | 0.16 | 3.79 | 50.96 | 0.00 | 6.47 | 0.30 | 84.73 | Partially corroded lead droplet |
| **6** | 34.97 | 0.06 | 0.48 | 49.60 | 0.00 | 7.63 | 0.13 | 92.87 | Partially corroded lead droplet |
| **7** | 85.75 | 0.91 | 10.23 | 0.21 | 0.00 | 0.00 | 0.00 | 97.10 | α phase |
| **8** | 83.29 | 0.71 | 13.26 | 0.26 | 0.00 | 0.01 | 0.00 | 97.51 | α phase |
| **9** | 55.71 | 0.32 | 0.00 | 1.70 | 0.00 | 0.45 | 0.03 | 58.21 | Malachite |
| **10** | 56.81 | 0.03 | 0.02 | 28.05 | 0.00 | 0.04 | 0.03 | 84.97 | Mixed corrosion of Cu & Pb |
| **11** | 18.50 | 2.34 | 32.66 | 30.92 | 0.00 | 2.48 | 0.06 | 81.96 | Mixed corrosion of Cu, Pb & Sn |
| **12** | 27.20 | 1.40 | 28.87 | 10.35 | 0.00 | 0.57 | 0.08 | 68.48 | Mixed corrosion of Cu, Pb & Sn |

BEI of the metallographic section shows a Pb-rich layer on the surface (Fig. 9). It seems to be cerussite based the XRD results

EPMA linescan across the black layer was carried out; the results are plotted in Fig. 10. Sulphur is richer in the black layer. Sn shows no difference from that in metal. Arsenic is richer in the black layer than that in other areas. Cl is slightly higher in the black layer than the metal although it is not much. Fe shows a correlation with Sn.

## SUMMARY

It is a ternary alloy of Cu-Sn-Pb with an equi-axed structure. The original composition is difficult to estimate because of corrosion. However, it seems that the original content of tin is in the range of 10-15%. The original lead content could be above 10% based on EPMA data and the presence of a Pb-rich layer on the surface. There is a black layer on the surface. Redeposited Cu is seen within cuprite.

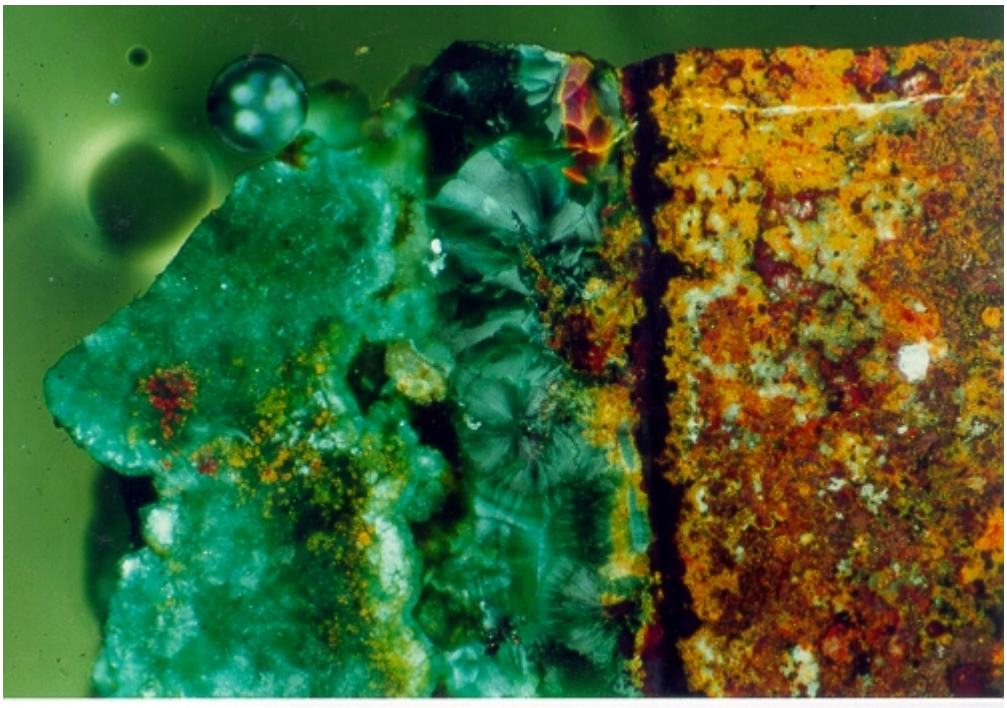


Fig. 6 Photomicrograph of the black layer.
C/P. Width of the image = 0.7 mm.

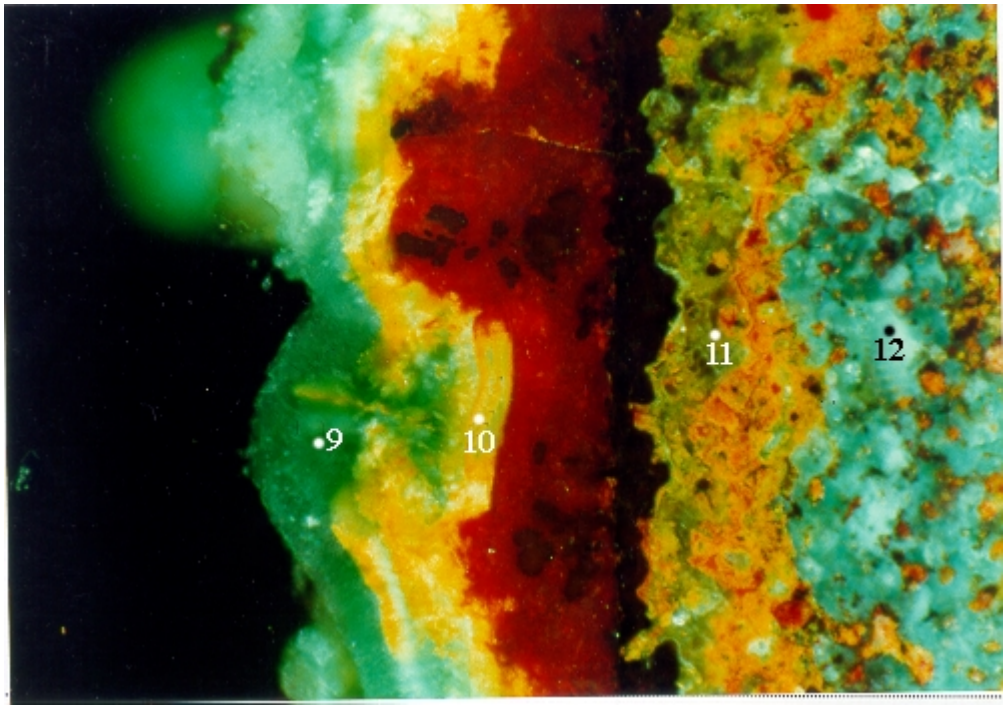



Fig. 7 Photomicrograph of corrosion layers, showing EPMA points.
C/P. Width of the image = 0.57 mm.

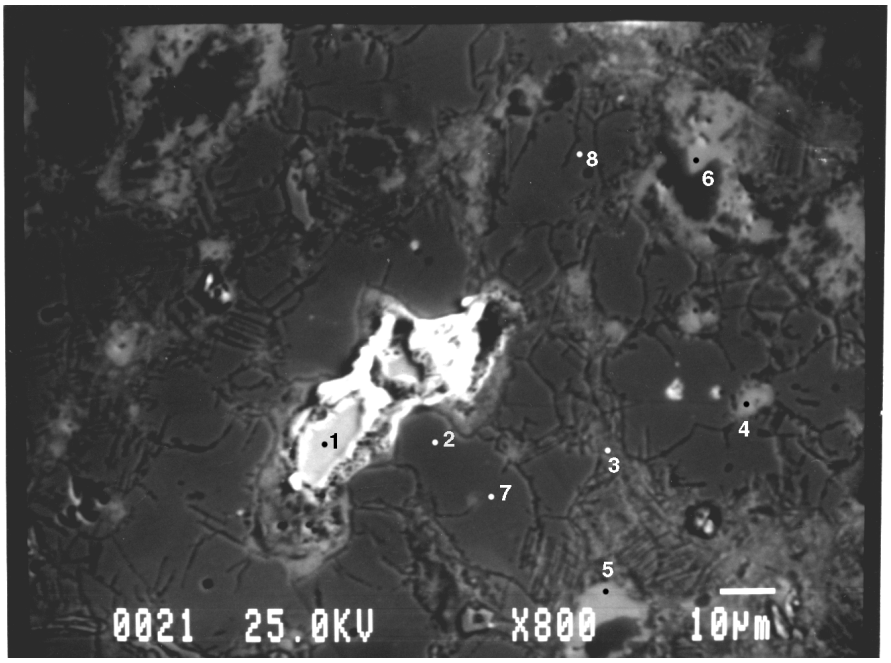



Fig. 8 SEM of metal, showing EPMA points.

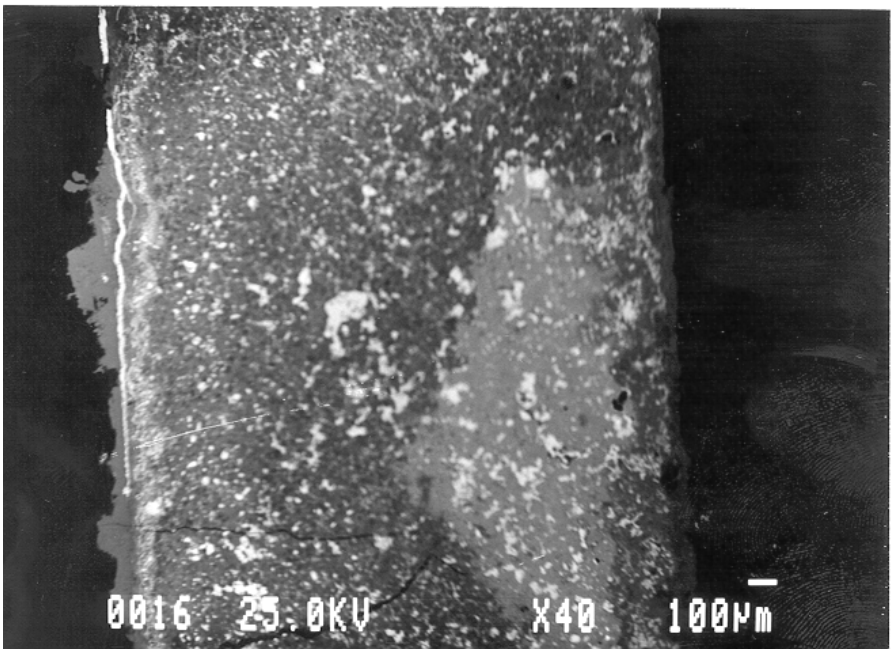



Fig. 9 BEI of the metallographic section, showing a Pb-rich layer on the surface to the left.

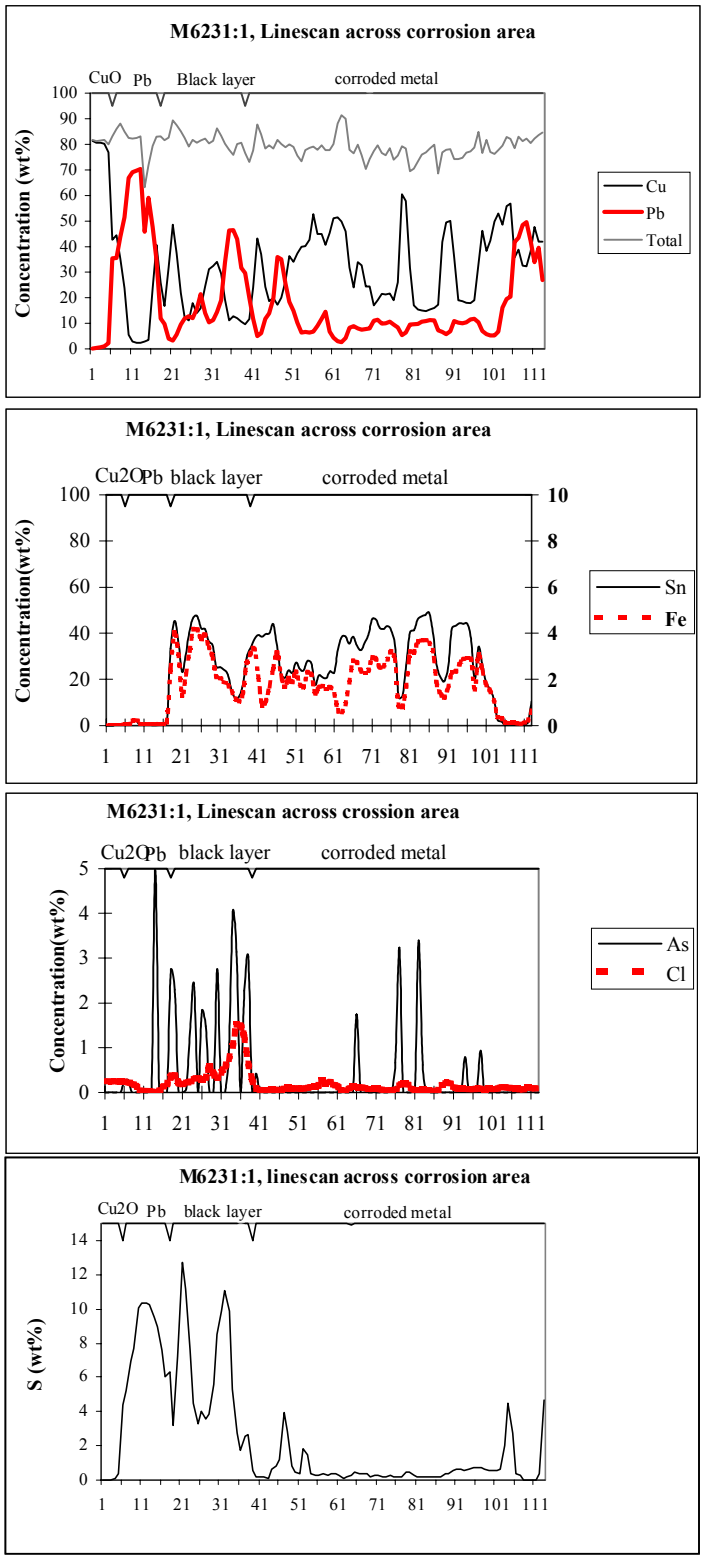



Fig. 10 EPMA lines across corrosion layers.

## GENERAL

**Object Number:** M6231:16
**Excavation Date:** 1984
**Origin:** Tianma-Qucun site

**Object:** vessel/*zeng*
**Date:** Early Western Zhou
**Fragment Weight:** 0.1 g
**Fragment size:** 4x3x1 mm

**General description:**

This fragment has all edges broken. Corrosion index is 1. Most parts of the surfaces but a corner are clean. That corner is covered with soil and corrosion products. No decoration is apparent.

## TECHNICAL STUDIES OF METAL

**Metallographic structure:**

The whole piece was mounted for metallographic observation. The estimated thickness is 1 mm as measured in the metallographic section. It has an equi-axed structure (Fig. 1). The estimated grain size is 0.031 mm. Pb globules are seen in the metal. Gas pores and shrinkage pores are also seen in the metal (Fig. 2).

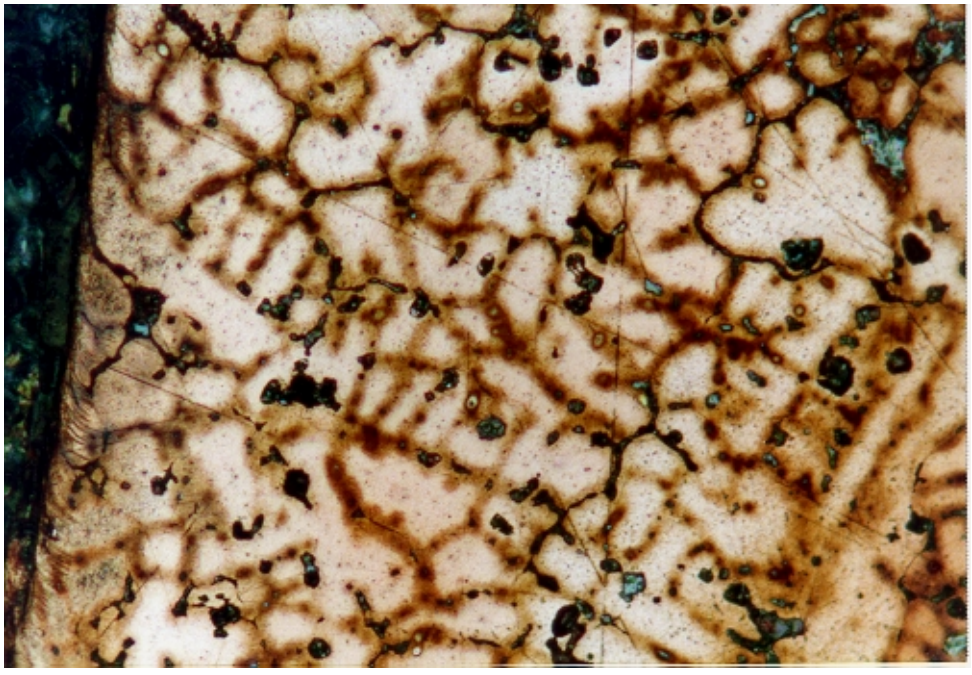


Fig. 1 Equi-axed microstructure of the metal. Etched in aqueous $FeCl_3$.
BF. Width of the image = 0.5 mm.

## Composition:

**AAS:** too small for sampling.

**Microanalysis:**

SEM/EDS semi-quantitative analysis was carried out on the metal, the results show that the distribution of Pb is not even. It can be taken as a copper object.

| Area 1(400x): | | | Area 2 (400x): | | | Area 3 (400X): | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Cu** | **Sn** | **Total** | **Cu** | **Sn** | **Total** | **Cu** | **Sn** | **Pb** | **Total** |
| 89.8 | 1.6 | 91.4 | 90.9 | 1.8 | 92.7 | 88.7 | 1.7 | 3.4 | 93.8 |

**Microhardness:** 66Hv

## CORROSION

**XRD results:** not carried out.

**Metallographic observation:**

In the corner with soil, quartz is dominant. Fe rich compound (the biggest grain in Fig. 3) is present in the soil. Cerussite (yellow layer in Fig. 4) is present as corrosion product. Charcoal is mixed with soil.

**Microanalysis:**

SEM/EDS qualitative analysis was carried out on the corner with soil, which confirmed the metallographic observations.

## SUMMARY

It is a copper object with inclusions of Sn and Pb. It has an equi-axed structure. It is well preserved; part of the surfaces is covered with soil and charcoal.

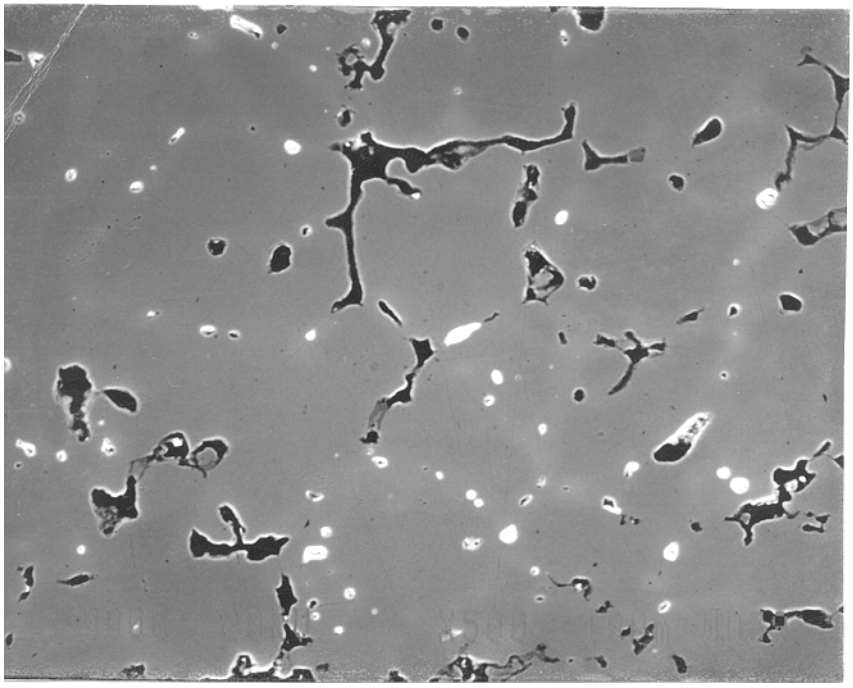


Fig. 2 BEI of the metal, showing the presence of Pb inclusions and pores.

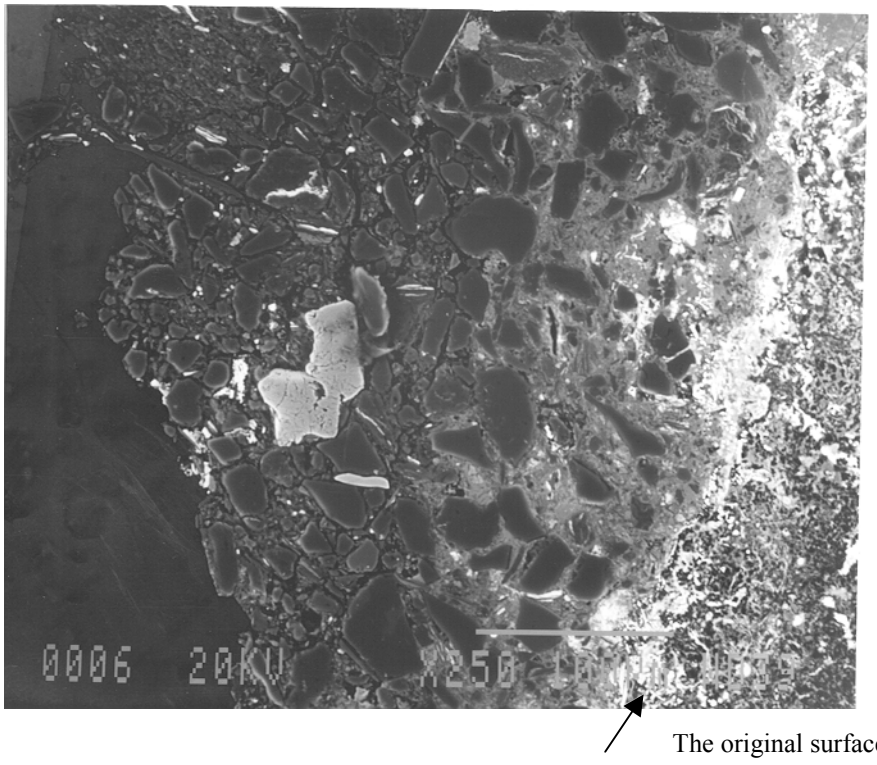



Fig. 3 BEI of corrosion overburden on the surface,
showing quartz and cerussite layer on the original surface.

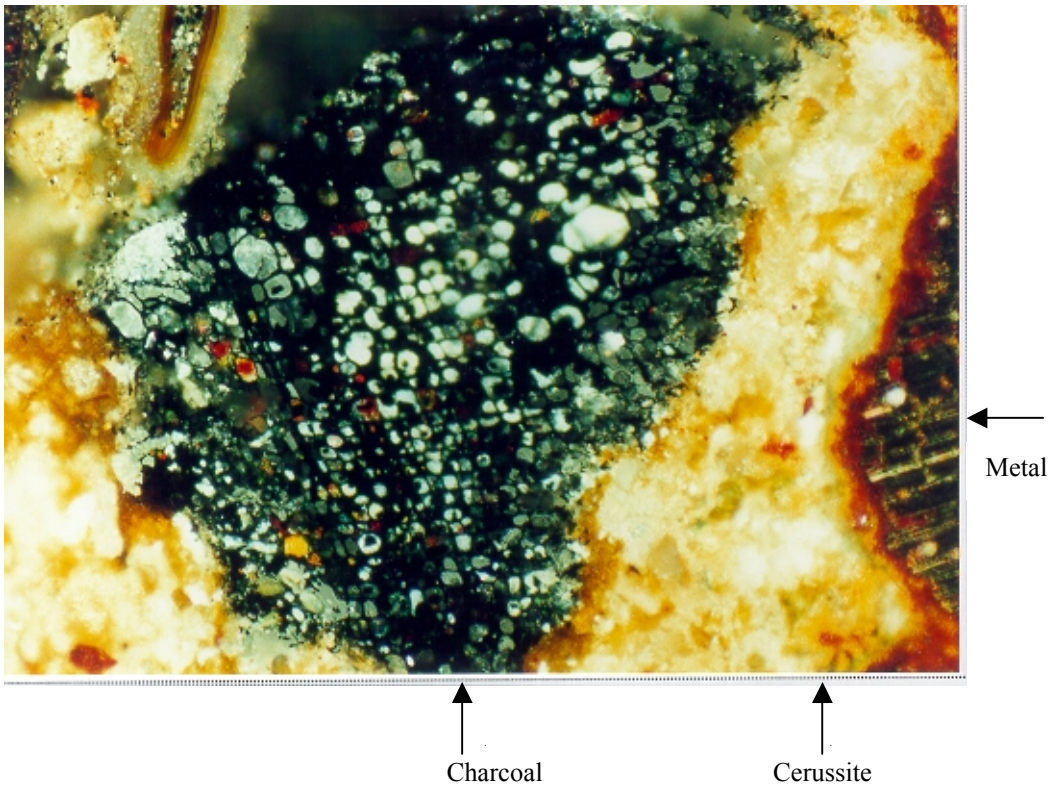



Fig. 4 Photomicrograph of charcoal and cerussite in corrosion overburden.
C/P. Width of the image = 0.7 mm.

## GENERAL

**Object Number:** M6231:31
**Excavation Date:** 1984
**Origin:** Tianma-Qucun site

**Object:** horse fitting/*luan* bell (Fig. 1)
**Date:** Early Western Zhou
**Fragment Weight:** 0.3 g
**Fragment size:** 12x3x1.4 mm

**General description:**

This fragment has all sides broken. Corrosion index is 5. There is a corrosion overburden on the surface, including mainly green corrosion products and soil. Black shinning materials are also observed. No decoration is apparent (Fig. 2)

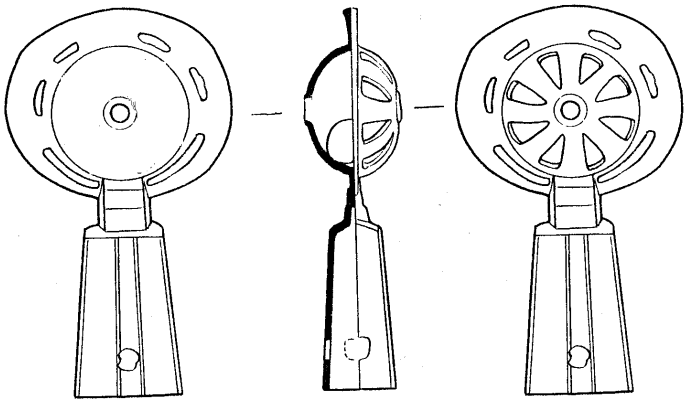


Fig. 1 The object

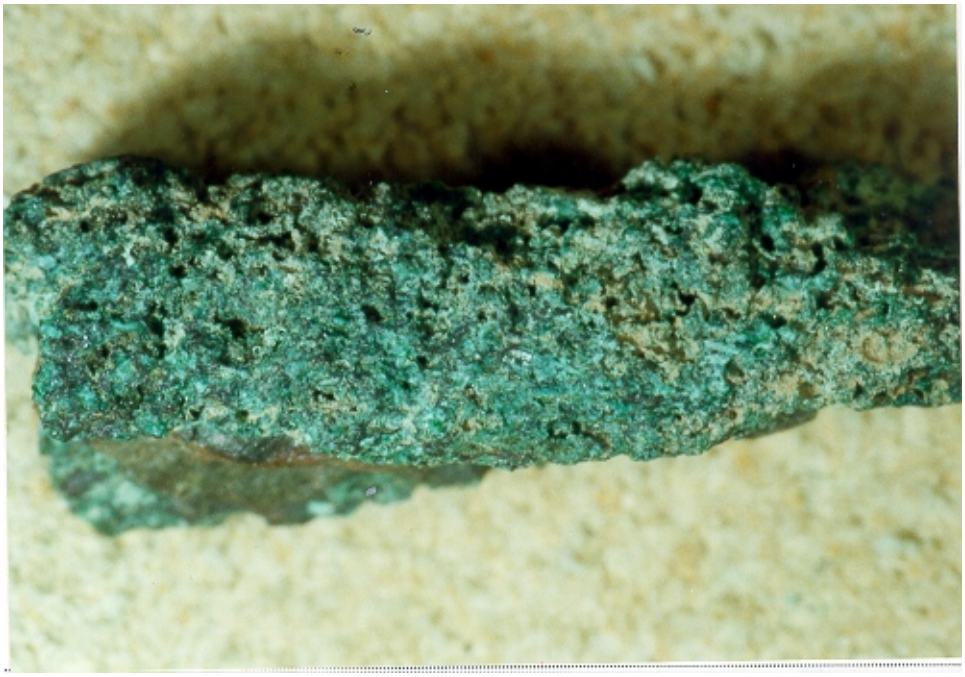


Fig. 2 General view of the fragment. Width of the image = 11 mm.

## TECHNICAL STUDIES OF METAL

### Metallographic structure:

A section cut through the full length of the fragment was taken for metallographic observation. The original surfaces can still be seen although the metal is totally corroded. The shape of the fragment shows that it was from a straight part, e.g. the stand, rather than from a sidewall or rim of the body. The estimated thickness is 1.4 mm as measured in the metallographic section. It has a dendritic structure (Fig. 3). The estimated dendritic arm spacing is 0.018 mm.

### Composition:

**AAS:** too corroded for analysis.

**Microanalysis:**

See corrosion section.

**Microhardness:** too corroded for measuring.

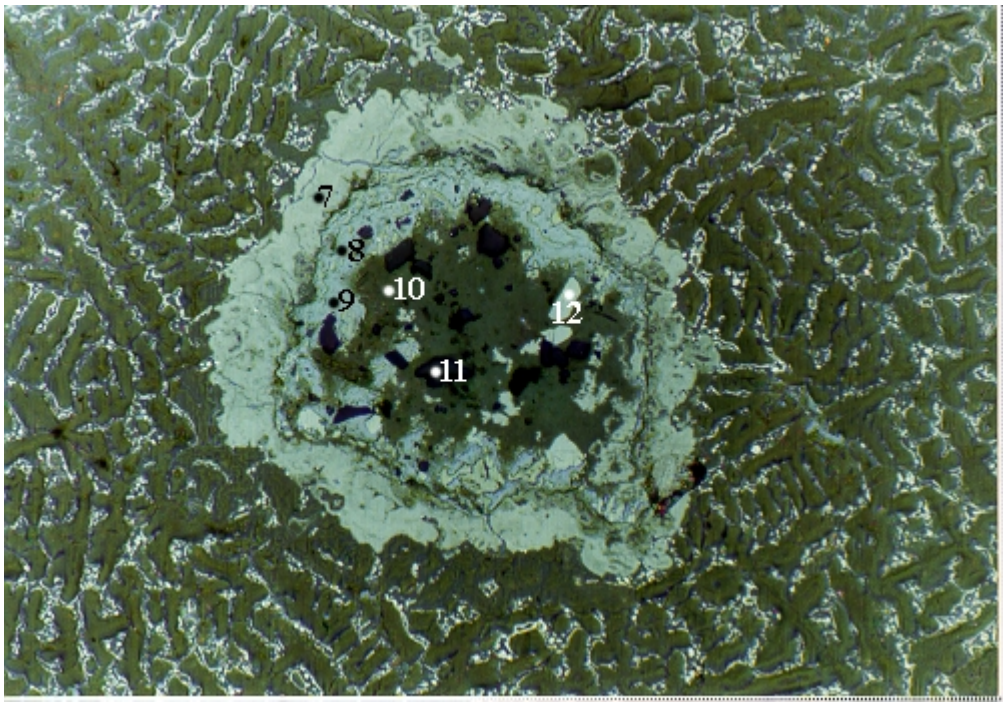



Fig. 3 Photomicrograph of a hole in metal, showing the presence of sulphide and cuprite. (EPMA points are shown ). BF. Width of the image = 0.57 mm.

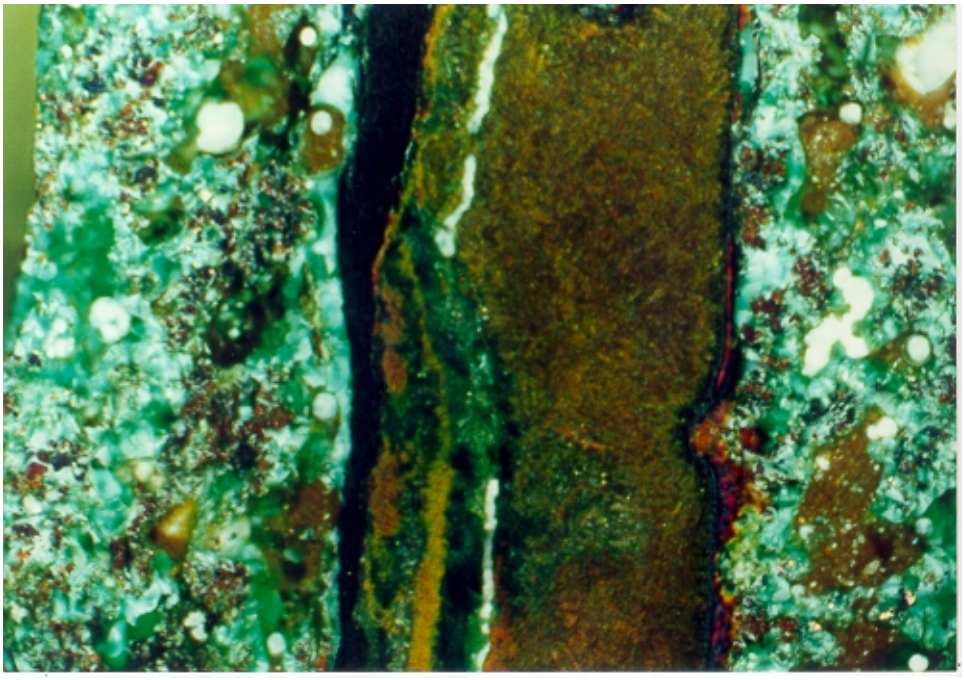


Fig. 4 Photomicrograph of cross section, showing black layers on the surface. C/P. Width of the image = 3.6 mm.

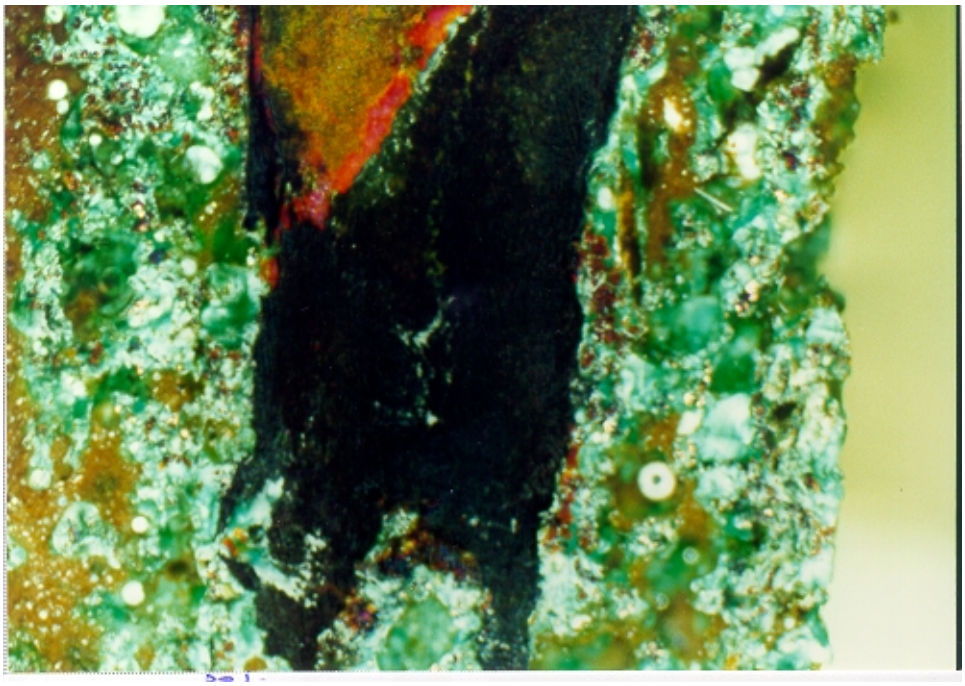


Fig. 5 Photomicrograph of another part of cross section, showing the whole section has been converted to black corrosion products. C/P. Width of the image = 3.6 mm.

## CORROSION

### XRD results:

Surface sample: malachite.

### Metallographic observation:

The whole piece is totally corroded; α phases have completely gone. There is a hole in the metal, which is about 300 μm in diameter (Fig. 3). It is sulphide at edge, and malachite with sulphide in the centre (see EPMA results below). There are black layers on both surfaces; one is thicker than the other (Fig. 4). The metal has completely converted to black corrosion products at one end of the section (Fig. 5). Corrosion overburden is up to 1.2 mm thick on both original surfaces, comprised of malachite, cuprite, sulphide, and probably cerussite, and soil.

### Microanalysis:

SEM semi-quantitative analysis was carried out on both the brown part and the black part of the corroded metal (Fig. 4); the results (shown below) show that sulphur is richer in the black part, while lead is richer in the brown part. Sn is over estimated because of corrosion.

Brown part (300x):

| Cu | Sn | Pb | Fe | Si | Total |
|---|---|---|---|---|---|
| 21.5 | 33.5 | 5.4 | 1.8 | 1.1 | 63.3 |

Black part (300x):

| Cu | Sn | Fe | S | Si | Total |
|---|---|---|---|---|---|
| 23.9 | 33.1 | 1.9 | 3.1 | 0.7 | 62.6 |

EPMA analysis was carried out on the corroded metal (Fig. 6) and the big hole (Fig. 3), the results are as follows:

| Point | Description |
|---|---|
| **1 – 6** | Corroded metal |
| **7 - 11** | The big hole, from the edge to the centre |
| **12** | A crystal in the hole, it is likely cuprite. |

| Point | Cu | Fe | Sn | Pb | As | S | Cl | Hg | total |
|---|---|---|---|---|---|---|---|---|---|
| **1** | 26.48 | 2.21 | 46.16 | 5.49 | 0.00 | 0.08 | 0.14 | 0.02 | 80.58 |
| **2** | 32.15 | 1.35 | 45.77 | 3.46 | 2.96 | 0.16 | 0.07 | 0.02 | 85.93 |
| **3** | 20.34 | 2.18 | 42.02 | 4.02 | 4.98 | 0.22 | 0.37 | 0.00 | 74.13 |
| **4** | 27.17 | 1.48 | 33.03 | 3.34 | 1.51 | 0.15 | 0.19 | 0.19 | 67.06 |
| **5** | 24.68 | 1.81 | 43.20 | 4.90 | 1.51 | 0.13 | 0.17 | 0.03 | 76.43 |
| **6** | 17.88 | 2.33 | 38.78 | 2.86 | 0.00 | 0.21 | 0.33 | 0.10 | 62.49 |
| **7** | 36.91 | 0.86 | 13.17 | 1.54 | 0.00 | 13.12 | 0.21 | 0.00 | 65.81 |
| **8** | 59.64 | 0.56 | 7.69 | 0.92 | 0.00 | 7.68 | 0.32 | 0.04 | 76.83 |
| **9** | 74.36 | 0.18 | 3.45 | 0.29 | 0.72 | 7.60 | 0.39 | 0.00 | 86.99 |
| **10** | 70.60 | 0.14 | 2.08 | 0.28 | 0.00 | 4.49 | 0.26 | 0.07 | 77.93 |
| **11** | 28.95 | 0.23 | 0.53 | 0.21 | 0.00 | 0.02 | 0.05 | 0.00 | 29.98 |
| **12** | 64.28 | 0.03 | 0.13 | 0.04 | 0.00 | 0.36 | 0.03 | 0.00 | 64.86 |

EPMA linescan across black layer was carried out, the result is plotted in Fig. 7. Several conclusions can be drawn from Fig. 7:

There is no obvious difference in tin content between the black layer and the other parts of the corroded metal. Sulphur is about 3% in the black layer but not represented in the metal. Chloride is a little higher in the black layer, which is up to 0.4%. Arsenic is found in the black layer and the other parts of the corroded metal. The highest content of As is 9.6% in the corroded metal. Fe is present in the whole specimen, without obvious difference between different areas, varying from 0.04 to 3.3%. Pb is also present in the whole piece with content varying between 0.1 - 6.1%.

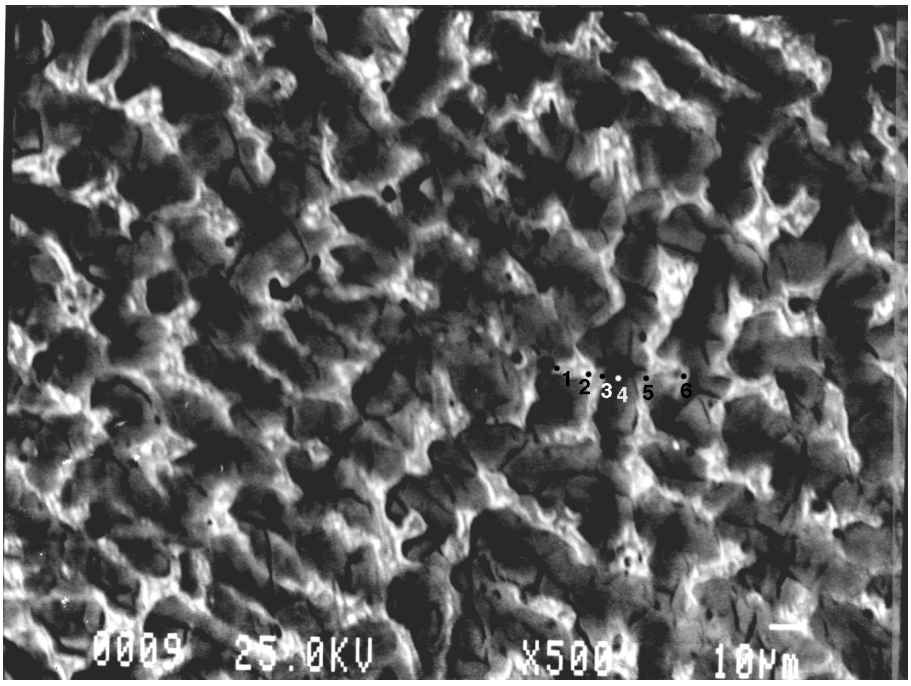



Fig. 6 BEI of corroded metal, showing EPMA points.

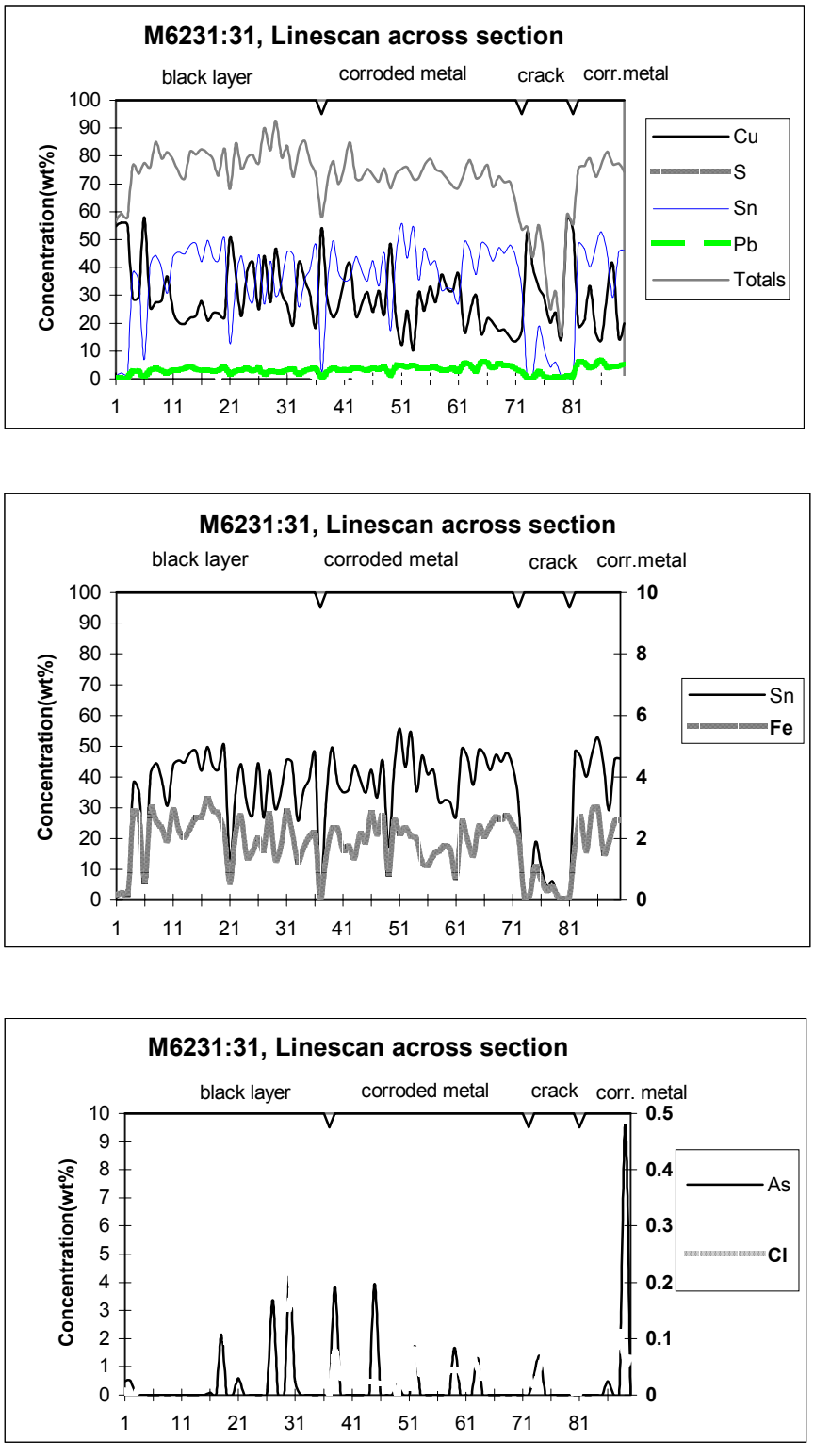



Fig. 7 EPMA linescan across the section, showing the correlation between Fe and Sn, and the enrichment of S in black layer

## SUMMARY

Microanalysis indicates that it is a ternary alloy of Cu-Sn-Pb. It has a dendritic structure. The original alloy composition is not estimated, because it is totally corroded. There is a thick corrosion overburden on the surface, comprising of malachite and sulphide. Black layers developed on the original surfaces with uneven thickness.

## GENERAL

**Object Number:** M6231:57
**Excavation Date:** 1984
**Origin:** Tianma-Qucun site

**Object:** bell (Fig. 1)
**Date:** Early Western Zhou
**Fragment Weight:** 0.1 g
**Fragment size:** 5x3x? mm

**General description:**

This fragment has all sides broken. Corrosion index is 5. The surface is covered with light green, green and black corrosion products and soil. Fibrous materials are also seen in the corrosion. No decoration is apparent.

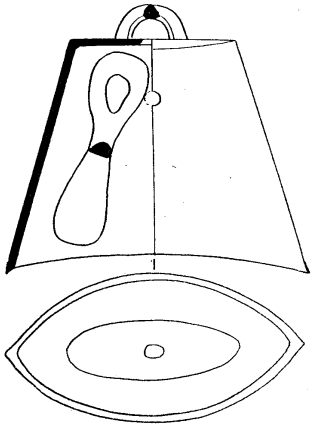


Fig. 1 The object

Fig. 2 The metallographic section. Length of the section = 5mm.

## TECHNICAL STUDIES OF METAL

### Metallographic structure:

The whole piece was mounted for metallographic observation. It is likely that this fragment is from a flat part of the object such as the sidewall. The original surfaces can not be seen because it is totally corroded and badly disrupted (Fig. 2). Therefore, its original dimension is not known. It has a dendritic structure (Fig. 3).

### Composition:

**AAS:** too corroded for analysis.

**Microanalysis:**

SEM/EDS semi-quantitative analysis was carried out on the corroded metal, the result shows it is a ternary alloy of Cu-Sn-Pb. The original composition is not estimated because of corrosion.

| Cu | Sn | Pb | Fe | Si | Cl | Total |
|---|---|---|---|---|---|---|
| 52.8 | 11.2 | 2.4 | 0.6 | 0.5 | 0.1 | 67.6 |

**Microhardness:** too corroded for measuring.

## CORROSION

**XRD results:** not carried out.

### Metallographic observation:

The whole piece is totally corroded with a only little isolated metallic phase being preserved. Large amounts of redeposited Cu are present (Fig. 3). Metal has mineralised to cuprite, cerussite, malachite etc. based on their characteristic colours in the metallographic section (Fig. 4).

**Microanalysis:** not carried out**.**

## SUMMARY

It is a ternary alloy of Cu-Sn-Pb with a dendritic structure. The original alloy composition is not estimated, because it is totally corroded. Redeposited Cu is present in the corroded metal.

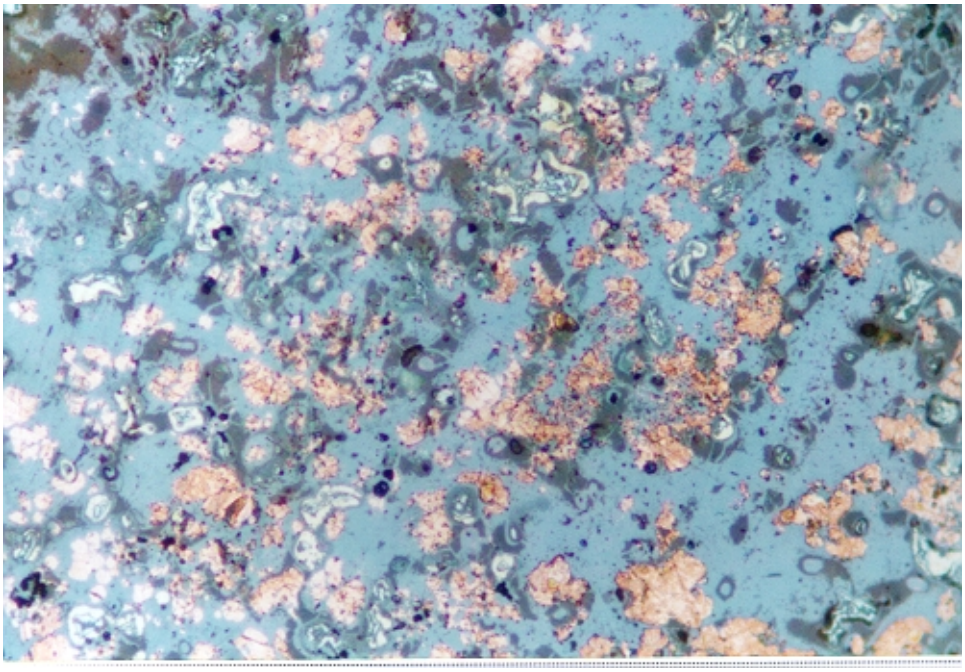


Fig. 3 Microstructure of corroded metal, showing remnant metallic phase and redeposited copper. BF. Width of the image = 0.2 mm.

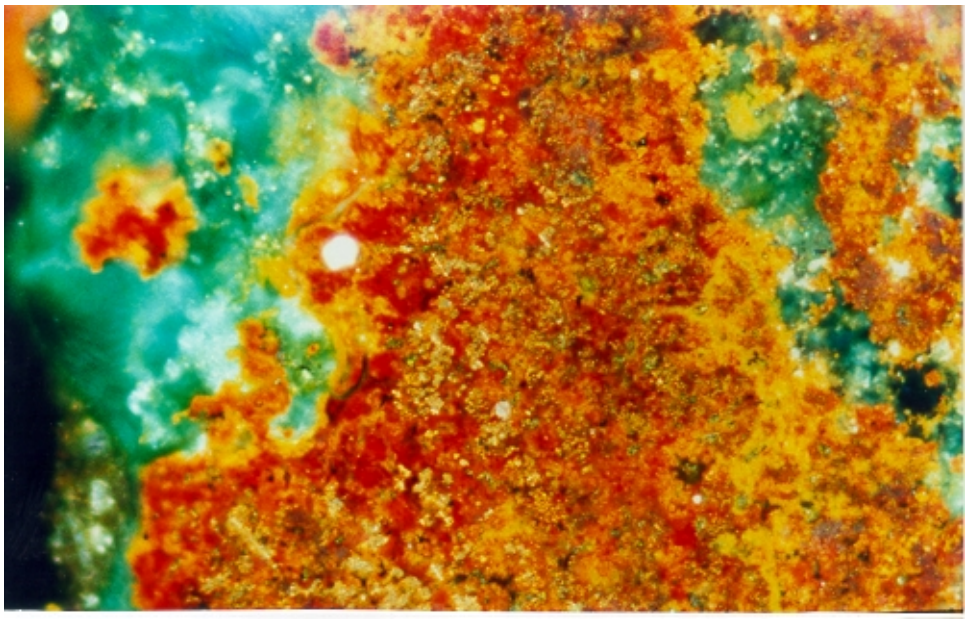


Fig. 4 Photomicrograph of the corroded metal, showing cuprite, copper carbonate and cerussite. C/P. Width of the image = 0.5 mm.

## GENERAL

**Object Number:** M6231:69(1)
**Excavation Date:** 1984
**Origin:** Tianma-Qucun site

**Object:** horse fitting/nose ornament
**Date:** Early Western Zhou
**Fragment Weight:** 0.7 g
**Fragment size:** 13x9x1.5 mm

**General description:**

Based on its shape this fragment is probably from one of the ends of the object. Corrosion index is 4. There is a corrosion overburden on the surface, including light green, green and red corrosion products and soil. Fibrous materials are also observed. No decoration is apparent (Fig. 1)

## TECHNICAL STUDIES OF METAL

**Metallographic structure:**

A section cut through the full length of the fragment was taken for metallographic observation. The original surfaces can still be seen although corrosion is deep (Fig. 2). The estimated thickness is 1.5 mm as measured in the metallographic section. It has a dendritic structure. Pb globules (up to 80 μm) (Fig. 3) indicate substantial amount of added lead in the original alloy. Sulphide inclusions are present.

**Composition:**

**AAS:** too corroded for analysis.

**Microanalysis:**

SEM semi-quantitative analysis was carried out on the metal, the results show an uneven distribution of lead.

Area 1 (300x):

| Cu | Sn | Pb | Total |
|---|---|---|---|
| 66.5 | 13.4 | 19.2 | 99.1 |

Area 2 (300x):

| Cu | Sn | Pb | Fe | Total |
|---|---|---|---|---|
| 68.2 | 14.3 | 15.3 | 0.3 | 98.1 |

**Microhardness:** 112Hv

Fig. 1 General view of the fragment.
Width of the image = 16mm.

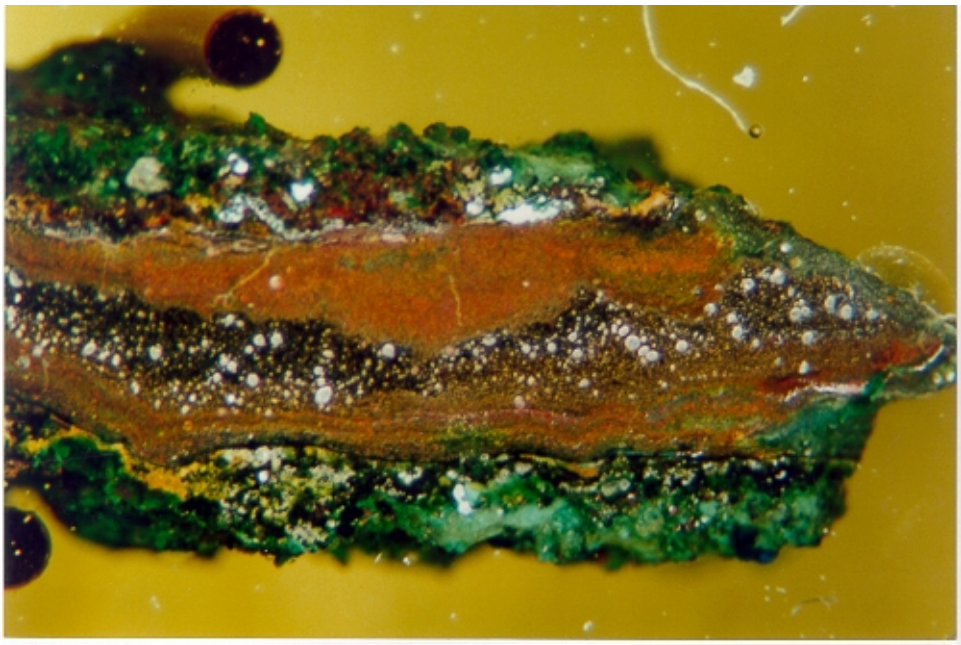


Fig. 2 The metallographic section.
Width of the image = 9mm.

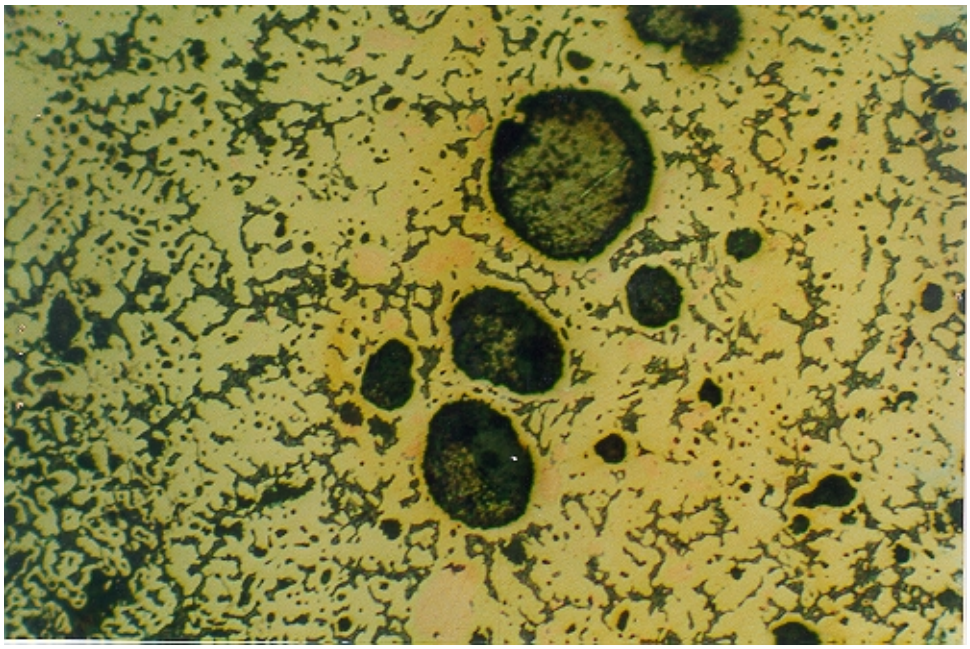


Fig. 3 Photomicrograph of Pb globules partially replaced by chloride.
BF. Width of the image = 0.5 mm.

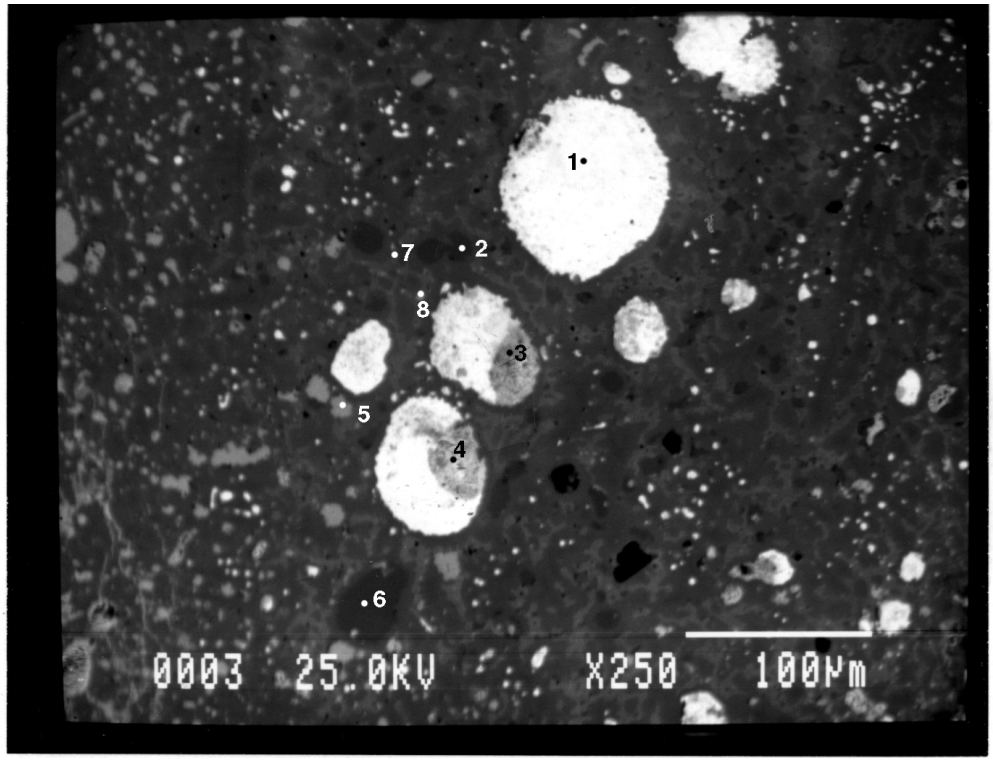



Fig. 4 BEI of Fig. 3, showing EPMA points.

## CORROSION

### XRD results:

Surface sample: cerussite, malachite.

### Metallographic observation:

In the centre of the piece, the δ phase has corroded away (Fig. 3). Redeposited Cu is present in this area but does not show twin lines. The corrosion overburden which is up to 1.25 mm thick on the surface mainly comprises of malachite and cerussite based on their characteristic colours in the metallographic section.

### Microanalysis:

EPMA was carried out on both metal (Fig. 4) and corrosion products (Fig. 5) on a surface; the results are as follow:

| Point | Description |
|---|---|
| **1** | Lead |
| **2, 7, 8** | α phase |
| **3, 4** | Corroded lead (replaced by chloride) |
| **5** | Sulphide inclusion |
| **6** | Redeposited copper |
| **9 - 16** | Corroded metal |
| **17, 18** | Corrosion overburden |

| Point | Cu | Ni | Fe | Sn | Pb | As | Zn | Co | S | Cl | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 0.28 | 0.00 | 0.08 | 0.03 | 100.47 | 0.00 | 0.00 | 0.00 | 0.00 | 0.09 | 100.95 |
| **2** | 85.84 | 0.01 | 0.22 | 13.51 | 0.13 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 99.71 |
| **3** | 2.45 | 0.02 | 0.08 | 0.15 | 53.12 | 0.00 | 0.00 | 0.01 | 0.00 | 11.88 | 67.71 |
| **4** | 0.75 | 0.00 | 0.06 | 0.00 | 47.19 | 1.51 | 0.00 | 0.01 | 0.00 | 7.27 | 56.80 |
| **5** | 4.85 | 0.00 | 0.03 | 0.66 | 52.26 | 0.00 | 0.00 | 0.00 | 8.52 | 0.05 | 66.38 |
| **6** | 98.72 | 0.00 | 0.01 | 0.03 | 0.06 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 98.82 |
| **7** | 78.86 | 0.01 | 0.10 | 15.60 | 1.07 | 0.00 | 0.00 | 0.00 | 0.05 | 0.01 | 95.70 |
| **8** | 85.35 | 0.01 | 0.11 | 13.47 | 0.04 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 98.98 |
| **9** | 47.15 | 0.02 | 0.09 | 33.40 | 4.52 | 0.00 | 0.00 | 0.00 | 0.07 | 0.09 | 85.34 |
| **10** | 9.56 | 0.00 | 0.06 | 7.33 | 56.43 | 0.00 | 0.00 | 0.00 | 7.32 | 0.16 | 80.85 |
| **11** | 28.88 | 0.02 | 0.18 | 13.33 | 36.68 | 0.06 | 0.00 | 0.00 | 4.80 | 0.24 | 84.18 |
| **12** | 70.62 | 0.00 | 0.04 | 6.81 | 11.60 | 0.00 | 0.00 | 0.00 | 2.46 | 0.11 | 91.63 |
| **13** | 4.30 | 0.02 | 0.29 | 15.89 | 63.75 | 0.00 | 0.00 | 0.02 | 0.00 | 0.10 | 84.37 |
| **14** | 30.76 | 0.01 | 1.87 | 28.64 | 12.50 | 2.38 | 0.00 | 0.00 | 0.01 | 0.09 | 76.26 |
| **15** | 47.78 | 0.01 | 1.41 | 23.76 | 6.02 | 0.00 | 0.00 | 0.00 | 0.10 | 0.13 | 79.21 |
| **16** | 21.18 | 0.01 | 1.53 | 28.77 | 7.52 | 2.00 | 0.00 | 0.01 | 1.06 | 0.01 | 62.09 |
| **17** | 63.18 | 0.00 | 0.04 | 0.04 | 1.07 | 0.00 | 0.00 | 0.00 | 10.54 | 0.01 | 74.88 |
| **18** | 53.80 | 0.00 | 0.03 | 0.69 | 0.87 | 0.00 | 0.00 | 0.00 | 4.18 | 0.00 | 58.95 |

## SUMMARY

It is a ternary alloy of Cu-Sn-Pb with a dendritic structure. The original composition is about 14% Sn and 15-19% Pb based on area analysis using SEM/EDS and EPMA point analysis. Some of Pb globules are attacked by chloride. Redeposited Cu is present in the metal.

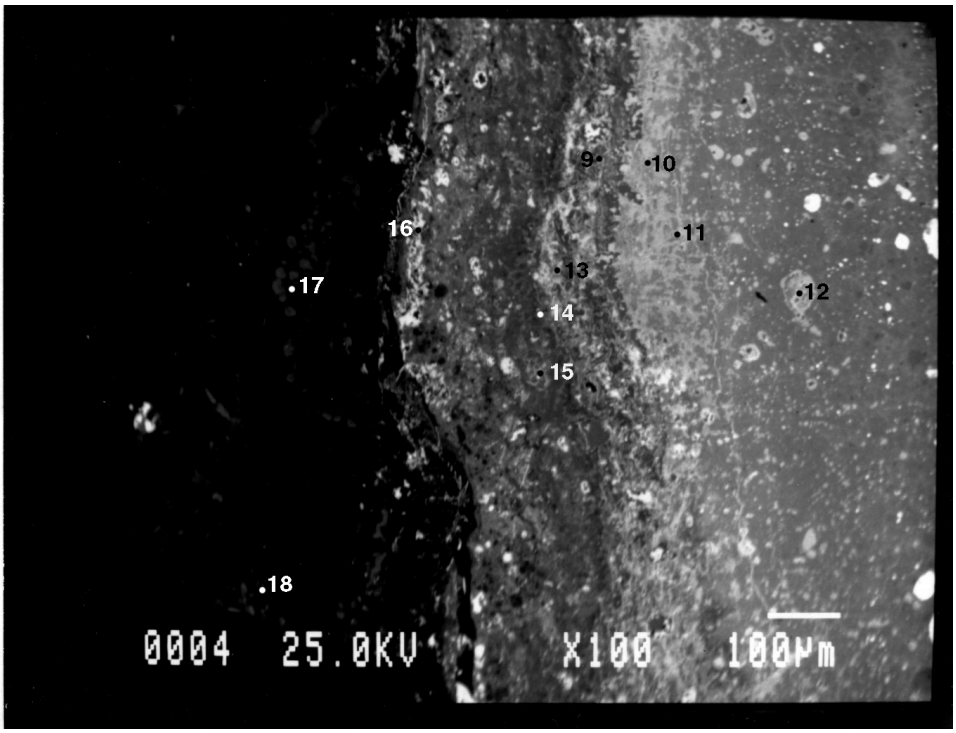



Fig. 5 BEI of corrosion products on surface, showing EPMA points.

## GENERAL

**Object Number:** M6231:69(2)
**Excavation Date:** 1984
**Origin:** Tianma-Qucun site

**Object:** horse fitting/*ma guan*
**Date:** Early Western Zhou
**Fragment Weight:** 0.4 g
**Fragment size:** 8x4x0.9 mm

**General description:**

This fragment has all sides broken. Corrosion index is 4. There is a corrosion overburden on the surface, including light green, green, red and black corrosion products. The powdery green material on the right of Fig.1 was suspected to be bronze disease. No decoration is apparent.

## TECHNICAL STUDIES OF METAL

**Metallographic structure:**

A section cut through the full length of the fragment was taken for metallographic observation. The original surfaces can be seen. The estimated thickness is 0.9 mm as measured in the metallographic section. It has a cast dendritic structure (Fig. 2). Pb globules can be seen. The estimated dendritic arm spacing is 0.016 mm.

**Composition:**

**AAS:** too corroded for analysis.

**Microanalysis:**

SEM/EDS semi-quantitative analysis was carried out on metal (300x), the result shows it is a ternary alloy of Cu-Sn-Pb.

| Cu | Sn | Pb | Total |
|---|---|---|---|
| 82.3 | 13.0 | 4.7 | 100.1 |

**Microhardness:** 120Hv

## CORROSION

**XRD results:**

The green material suspected to be bronze disease: malachite.

**Metallographic observation:**

The metal at both ends is badly corroded, with δ phases being preserved at one end (Fig. 3), but α phases preserved at the other (Fig. 4). There is a very thin black layer (about 20 μm) on one surface. Corrosion overburden is mainly comprised of malachite based on its characteristic colour in the metallographic section. Copper sulphide is also present in the corrosion overburden.

**Microanalysis:** not carried out

**SUMMARY**

It is a ternary alloy of Cu-Sn-Pb with a dendritic structure. The best estimated bulk composition conducted by SEM/EDS is 82% Cu, 13% Sn and 5% Pb. Two types of corrosion: α-removal and δ-removal corrosion are observed in this sample. A very thin black layer and copper sulphide is present in corrosion on the surface.

Fig. 1 General view of the fragment. Height of the image = 8mm.

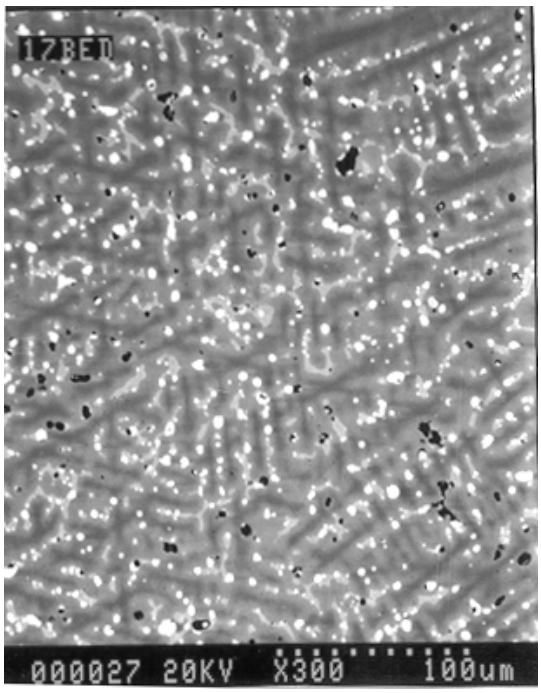



Fig. 2 BEI of dendritic structure.

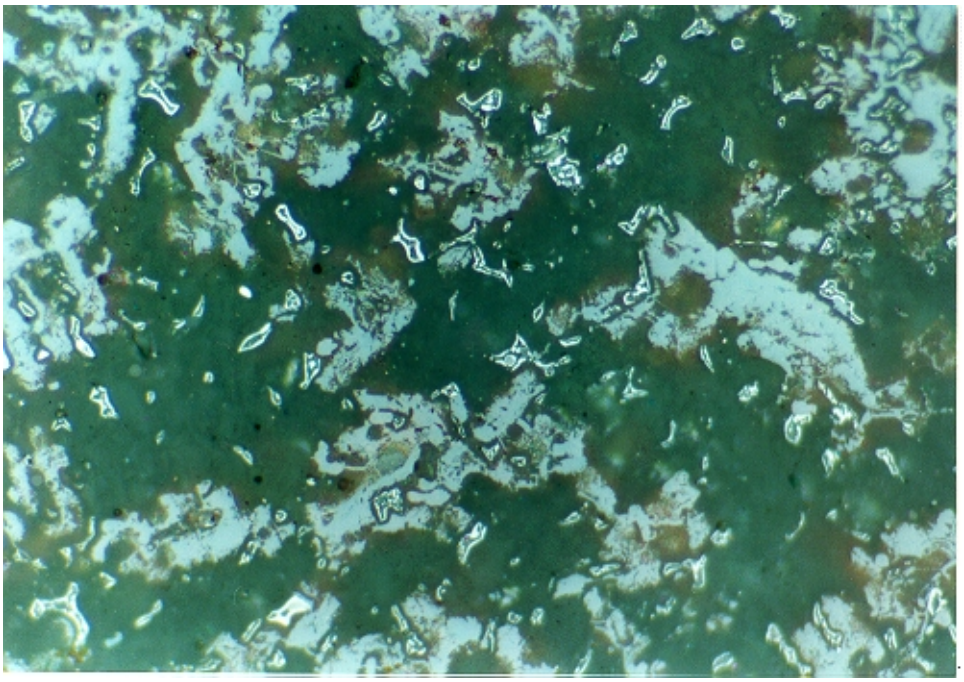


Fig. 3 Photomicrograph of α-removal area.
BF. Width of the image = 0.28 mm.

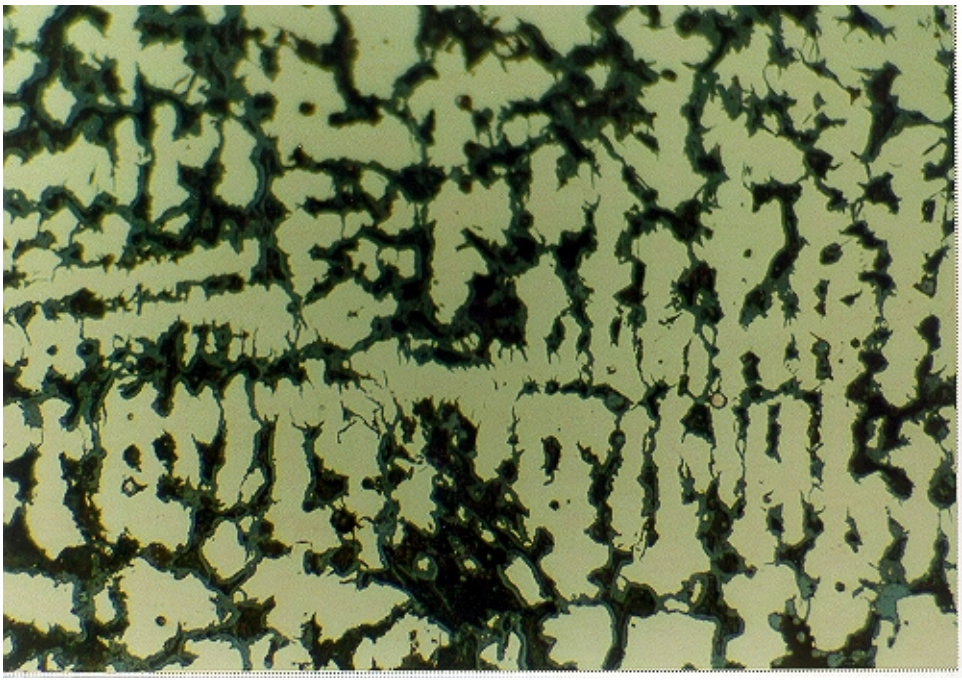


Fig. 4 Photomicrograph of δ-removal area.
BF. Width of the image = 0.28 mm.

## GENERAL

**Object Number:** M6231:69(3)
**Excavation Date:** 1984
**Origin:** Tianma-Qucun site
**Object:** horse fitting/harness
**Date:** Early Western Zhou
**Fragment Weight:** 0.3 g
**Fragment size:** 7x5x2 mm

**General description:**

This fragment has all sides broken and is very porous. Corrosion index is 5. There is a corrosion overburden on the surface, including light green and green corrosion products and soil. Many holes are seen on the surface. No decoration is apparent.

## TECHNICAL STUDIES OF METAL

**Metallographic structure:**

A section cut through the full length of this fragment was taken for metallographic observation. The original surfaces are badly disrupted. The estimated thickness is 2 mm as measured in the metallographic section. It has a dendritic structure (Fig. 1).

**Composition:**

**AAS:** too corroded for analysis.

**Microanalysis:**

SEM/EDS semi-quantitative analysis was carried out on the corroded metal, the result is as follows:

| Cu | Sn | Pb | Fe | Si | Total |
|---|---|---|---|---|---|
| 35.0 | 20.4 | 5.3 | 1.0 | 0.9 | 62.6 |

The original composition is not estimated, because it is totally corroded. SEM/EDS data just gives one an idea that it was a leaded bronze. The figure of Sn is higher than the original tin content, while Cu and Pb are lower than the original contents because they are more soluble than tin oxide.

**Microhardness:** too corroded for measuring.

## CORROSION

**XRD results:** not carried out.

**Metallographic observation:**

The whole piece is totally corroded, with some δ phases being preserved. α phases have completely gone (Fig. 1). Redeposited Cu is seen in cuprite (Fig. 1). There is a black layer on one surface (Fig. 2). Large amounts of copper sulphides are seen in the corrosion overburden (Fig. 3). Charcoal is seen on one surface (Fig. 4).

**Microanalysis:** not carried out

## SUMMARY

It is a ternary alloy of Cu-Sn-Pb with a dendritic structure. The original composition is not estimated, because it is totally corroded. Copper sulphide is present in the corrosion. There is a black layer on one surface. Redeposited Cu is present within cuprite.

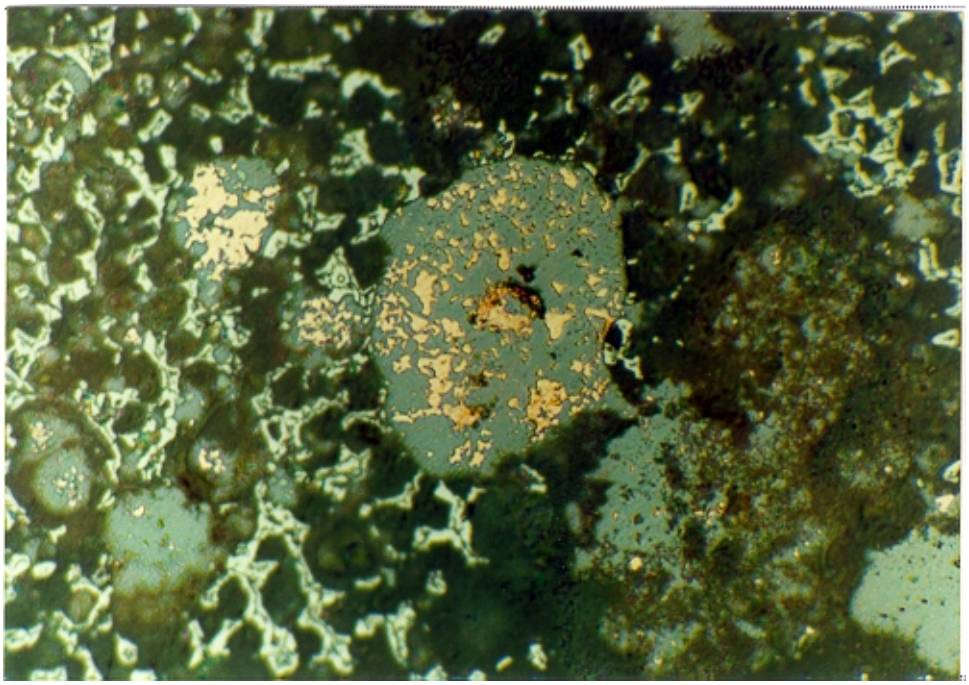


Fig. 1 Dendritic microstructure of corroded metal, showing redeposited Cu within cuprite.
BF. Width of the image = 0.15 mm.

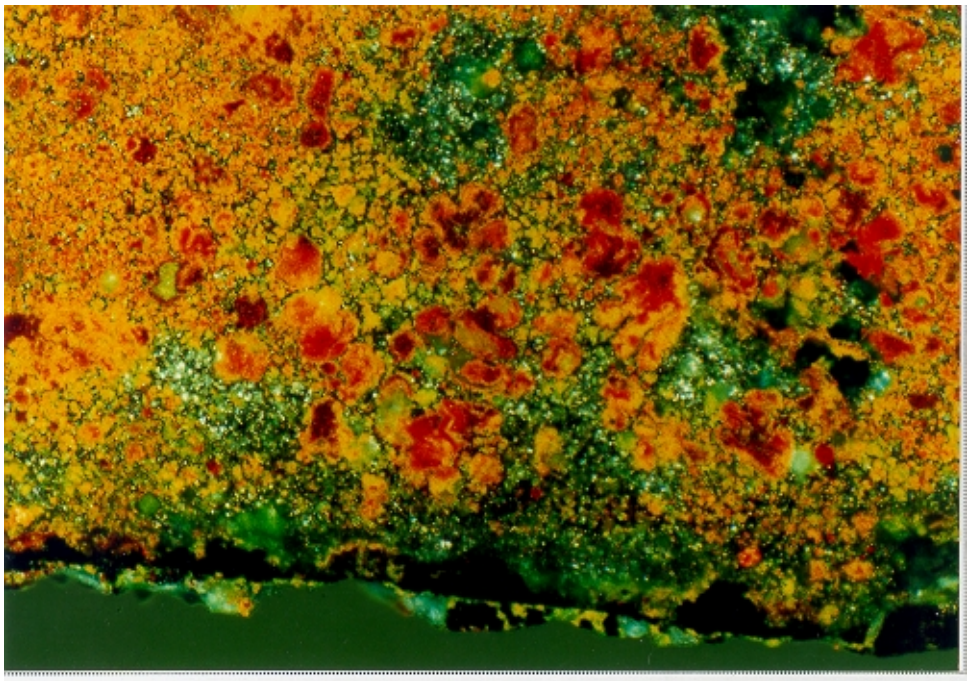


Fig. 2 Photomicrograph of black layer on surface.
C/P. Width of the image = 0.7 mm.

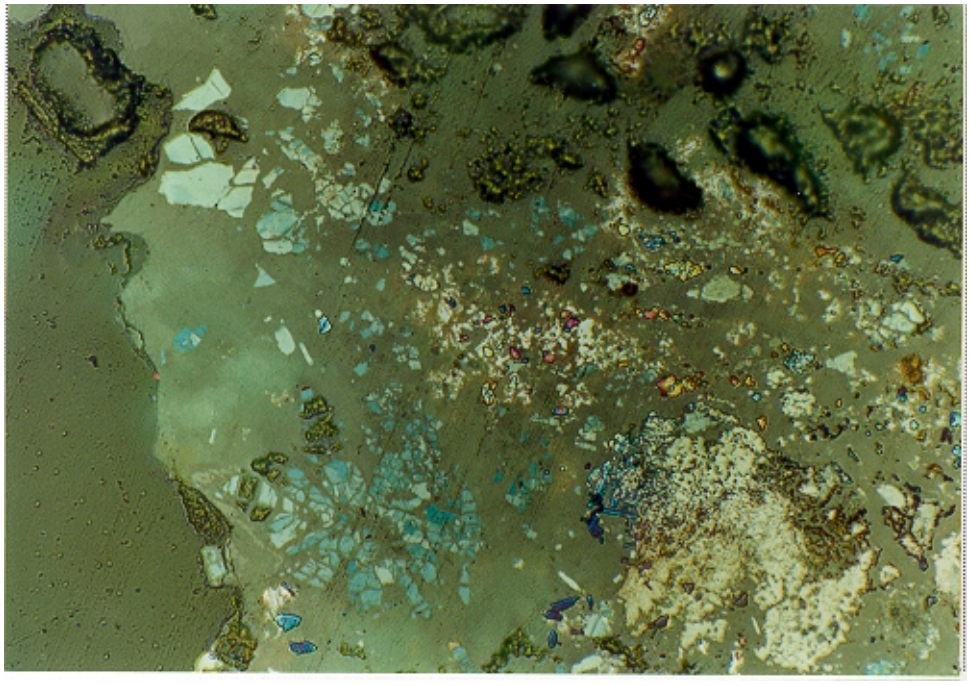


Fig. 3 Photomicrograph of sulphides in corrosion overburden.

BF. Width of the image = 0.28mm.

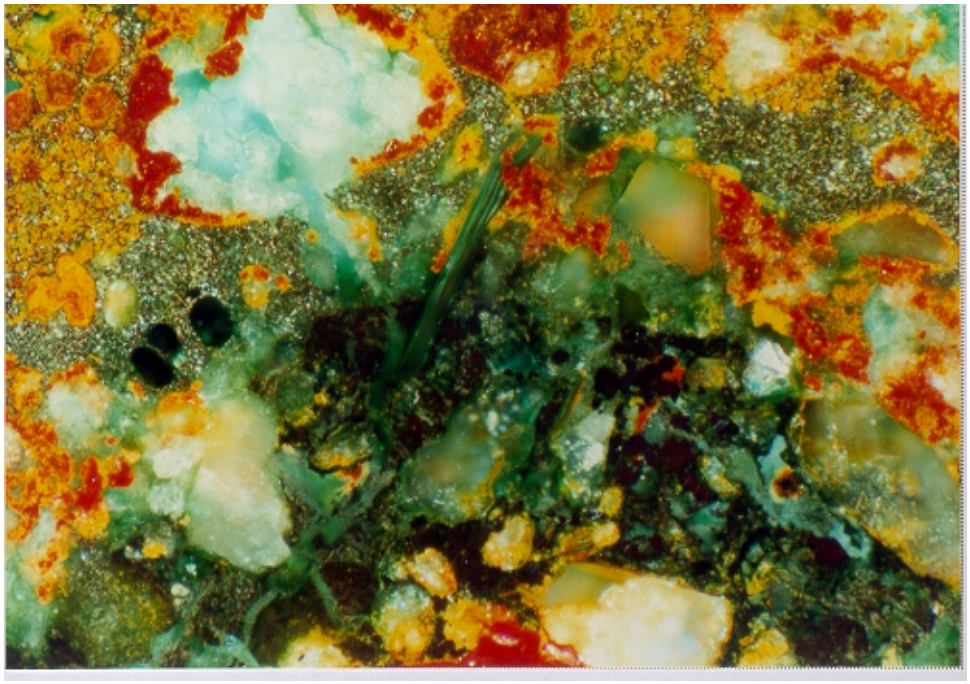


Fig. 4 Photomicrograph of charcoal on surface.

C/P. Width of the image = 0.7 mm.

## GENERAL

**Object Number:** M6231:71
**Object:** bell
**Excavation Date:** 1984
**Date:** Early Western Zhou
**Origin:** Tianma-Qucun site
**Fragment Weight:** 1.0 g
**Fragment size:** 12x10x? mm

**General description:**

This fragment has all sides broken. Corrosion index is 5. There is a corrosion overburden on the surface, including light green, green and black corrosion products and soil. Nodular malachite is dominant. No decoration is apparent (Fig. 1)

## TECHNICAL STUDIES OF METAL

**Metallographic structure:**

A section cut through the full length of the fragment was taken for metallographic observation. Part of the original surfaces can still be seen (Fig. 2). The shape of the section suggests that it was from a bottom corner between the side and bottom edges (see Fig. 1 of M6231:57). It is almost totally corroded with only a small area of metal being left (Fig. 3). It has a dendritic structure with large amounts of Pb.

**Composition:**

**AAS:** too corroded for analysis.

**Microanalysis:**

SEM/EDS semi-quantitative analysis was carried out on both metal and corroded metal; the results are as follows:

Metal (300x):

| Cu | Sn | Pb | Total |
|---|---|---|---|
| 79.0 | 8.9 | 8.3 | 96.2 |

Corroded metal (300x):

| Cu | Sn | Pb | Si | Fe | Total |
|---|---|---|---|---|---|
| 59.5 | 14.9 | 3.8 | 0.6 | 0.7 | 79.5 |

Above results show that Sn is richer in the corroded area than that in the metal, but Cu and Pb are both lower than that in metal. Because the corrosion of Cu and Pb are more soluble than that of Sn.

**Microhardness:** 85Hv

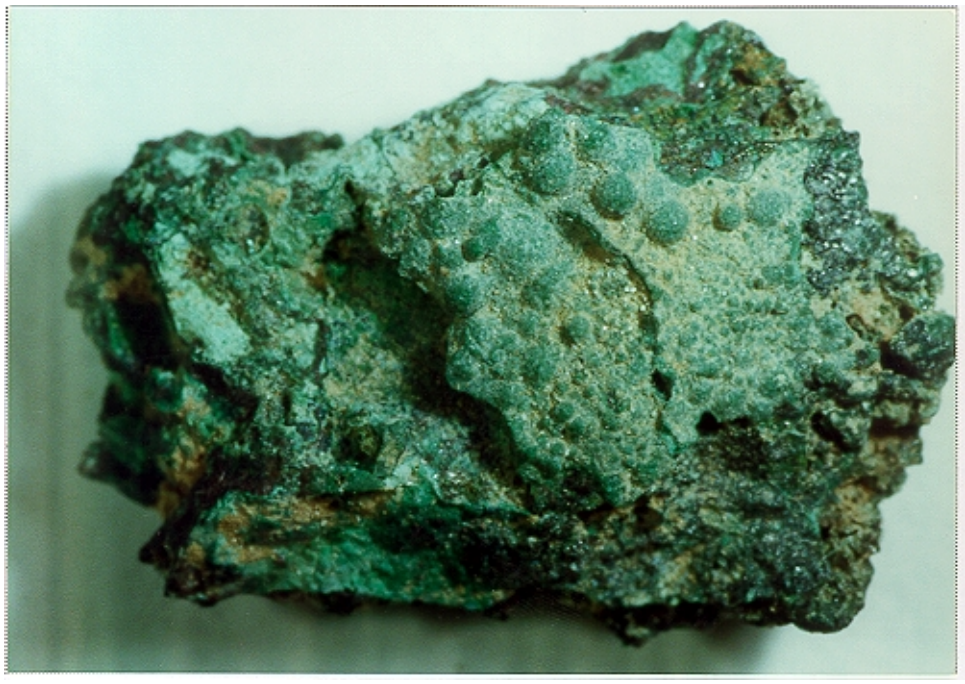


Fig. 1 General view of the fragment.
Width of the image = 14 mm.

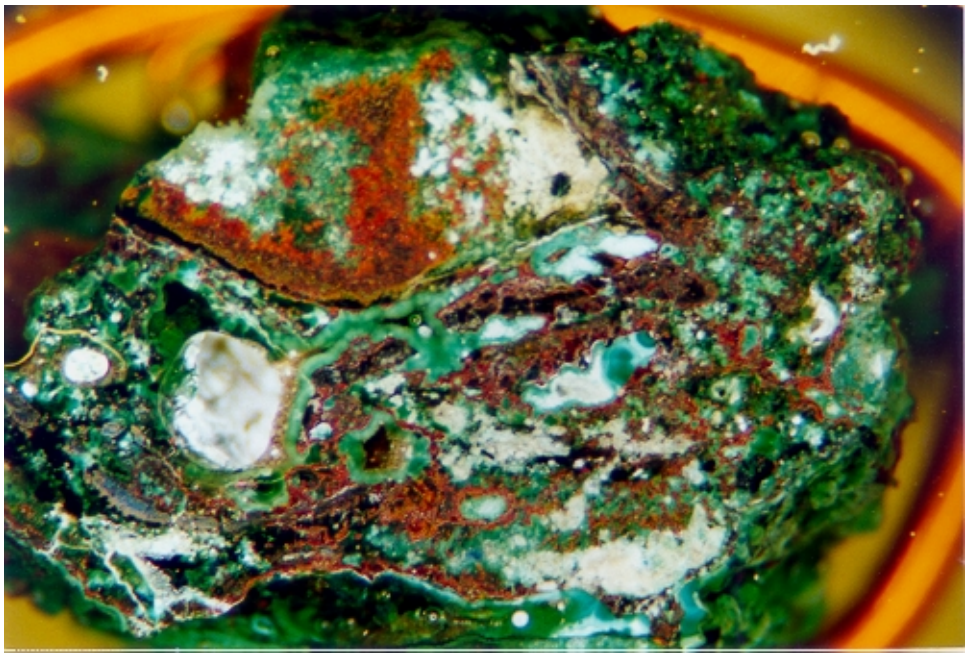


Fig. 2 The metallographic section, showing a thick corrosion overburden.
Width of the image = 9 mm.

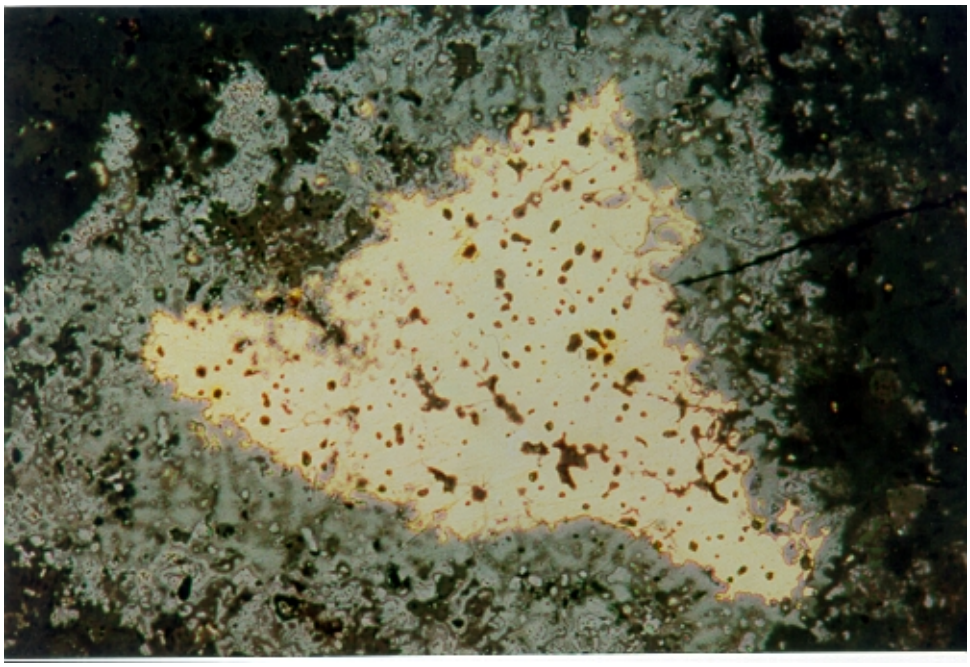


Fig. 3 Photomicrograph of remnant metal.
BF. Width of the image = 0.5 mm

## CORROSION

### XRD results:

Surface sample: malachite, cerussite.

### Metallographic observation:

Corrosion overburden is about 3 mm thick. There are malachite, cuprite, and copper sulphide in the corrosion overburden based on their characteristic colours in the metallographic section. There is a black layer on the original surface (Fig. 2).

### Microanalysis:

EPMA was carried out on corrosion; the results are as follow (Figs. 4 & 5):

| Point | Description |
|---|---|
| **1** | Cuprite |
| **2, 3, 4** | Copper sulphide / sulphate |
| **5** | Cerussite |
| **6, 7, 8** | Copper carbonate |
| **9, 10, 11** | Mixed corrosion of Cu, Sn, Pb in the inner layer of corrosion overburden |

| Point | Cu | Fe | Sn | Pb | As | S | Cl | Hg | Sb | Bi | Ag | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 83.11 | 0.04 | 0.00 | 0.23 | 0.00 | 0.18 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 83.56 |
| **2** | 63.93 | 0.01 | 0.34 | 0.00 | 0.00 | 20.81 | 0.00 | 1.68 | 0.00 | 0.00 | 0.01 | 86.78 |
| **3** | 60.07 | 0.00 | 0.04 | 0.00 | 0.00 | 20.07 | 0.00 | 0.58 | 0.00 | 0.08 | 0.00 | 80.84 |
| **4** | 46.93 | 0.01 | 0.02 | 0.02 | 0.00 | 16.64 | 0.00 | 0.00 | 0.00 | 0.02 | 0.05 | 63.69 |
| **5** | 1.91 | 0.06 | 0.01 | 73.76 | 0.00 | 0.00 | 0.03 | 0.00 | 0.00 | 0.00 | 0.00 | 75.76 |
| **6** | 59.02 | 0.02 | 0.01 | 1.43 | 0.00 | 0.06 | 0.00 | 0.00 | 0.01 | 0.00 | 0.02 | 60.56 |
| **7** | 51.79 | 0.02 | 0.02 | 0.94 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.03 | 52.79 |
| **8** | 53.11 | 0.07 | 0.27 | 2.61 | 0.00 | 0.02 | 0.00 | 0.00 | 0.00 | 0.01 | 0.05 | 56.12 |
| **9** | 14.22 | 2.99 | 40.41 | 10.85 | 0.00 | 0.16 | 0.05 | 0.00 | 0.00 | 0.22 | 0.00 | 68.90 |
| **10** | 34.78 | 1.63 | 24.16 | 6.45 | 0.00 | 0.21 | 0.01 | 0.00 | 0.00 | 0.06 | 0.01 | 67.31 |
| **11** | 46.19 | 1.24 | 12.13 | 5.65 | 0.00 | 0.19 | 0.01 | 0.00 | 0.00 | 0.30 | 0.07 | 65.79 |

## SUMMARY

It is a ternary alloy of Cu-Sn-Pb with a dendritic structure. The best estimate of bulk composition determined by SEM/EDS is 79% Cu, 9% Sn and 8% Pb. There is a black layer on the surface. Malachite and copper sulphide are the main corrosion products on the surface.

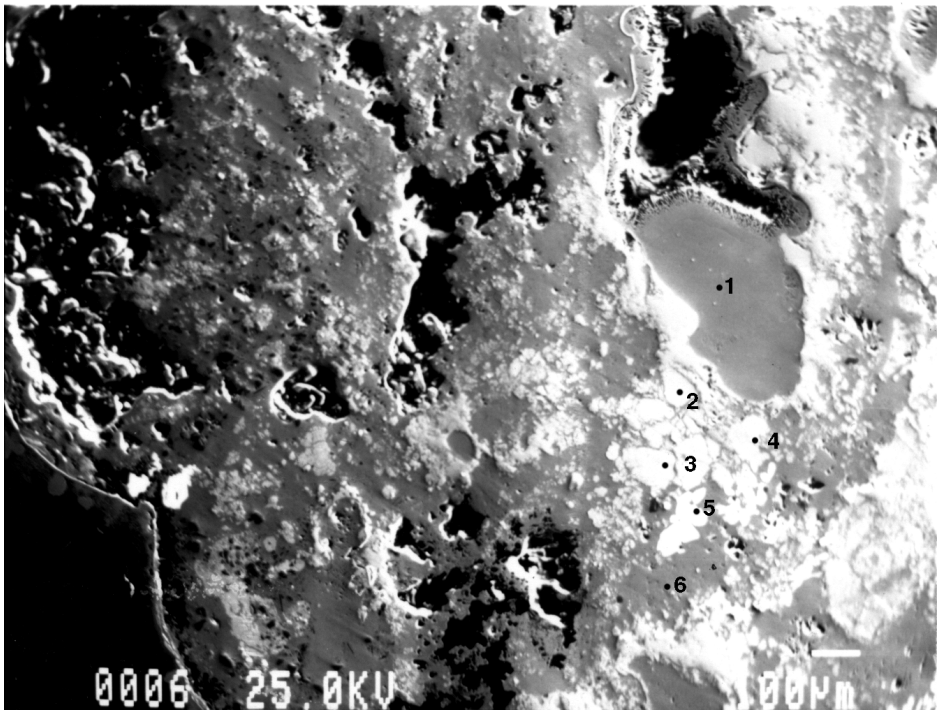



Fig. 4 SEI of corrosion products in the outer layer of the corrosion overburden, showing EPMA points.

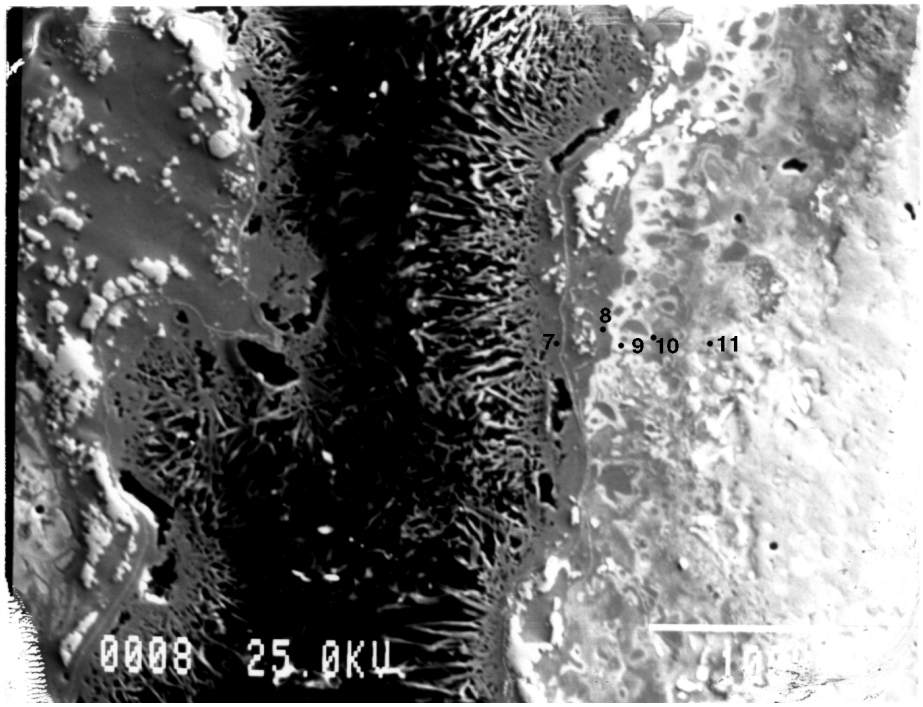



Fig. 5 SEI of corrosion products in the inner layer of the corrosion overburde, showing EPMA points.

## GENERAL

**Object Number:** M6231:73
**Excavation Date:** 1984
**Origin:** Tianma-Qucun site

**Object:** horse fitting/*luan* bell
**Date:** Early Western Zhou
**Fragment Weight:** 1.0 g
**Fragment size:** 12x9x1.8 mm

**General description:**

This fragment has all sides broken. Corrosion index is 5. There is a corrosion overburden on the surface, including green, black and blue corrosion products and soil. Fibrous materials are also observed in the corrosion. No decoration is apparent (Fig. 1).

## TECHNICAL STUDIES OF METAL

**Metallographic structure:**

The whole piece was mounted for metallographic observation. The original surfaces can still be seen although the metal is totally corroded. The estimated thickness is 1.8 mm as measured in the metallographic section. The shape of the fragment indicates that it was from the sidewall or rim of the body rather than from the stand. A pseudomorphic dendritic structure can be seen (Fig. 2).

Fig. 1 The metallographic section. BF. The thickness of the original metal is about 1.8 mm.

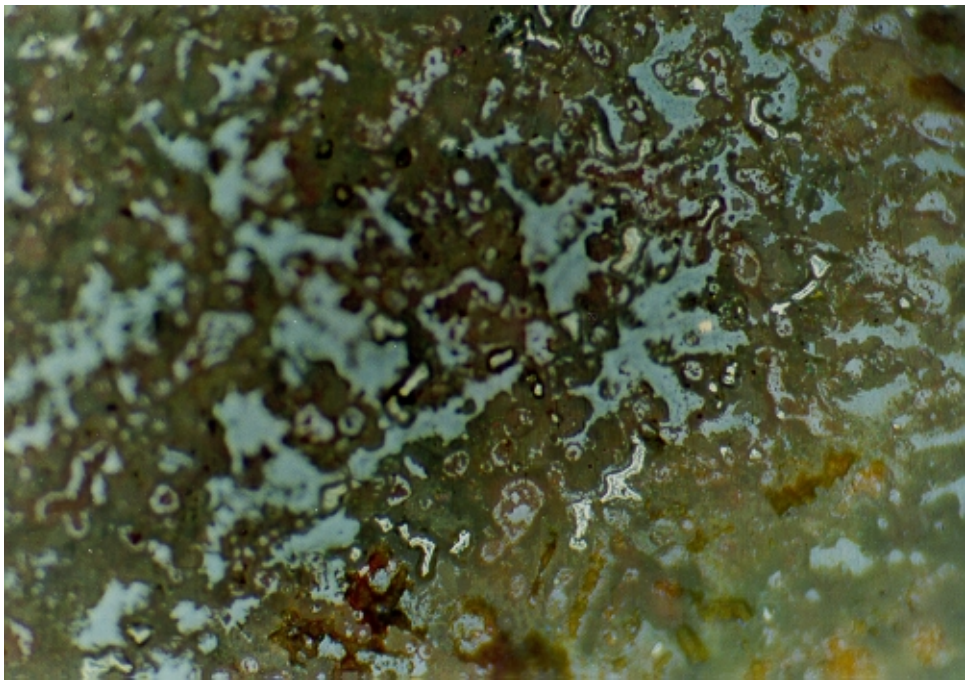


Fig. 2 Dendritic structure of corroded metal.

BF. Width of the image = 0.28 mm.

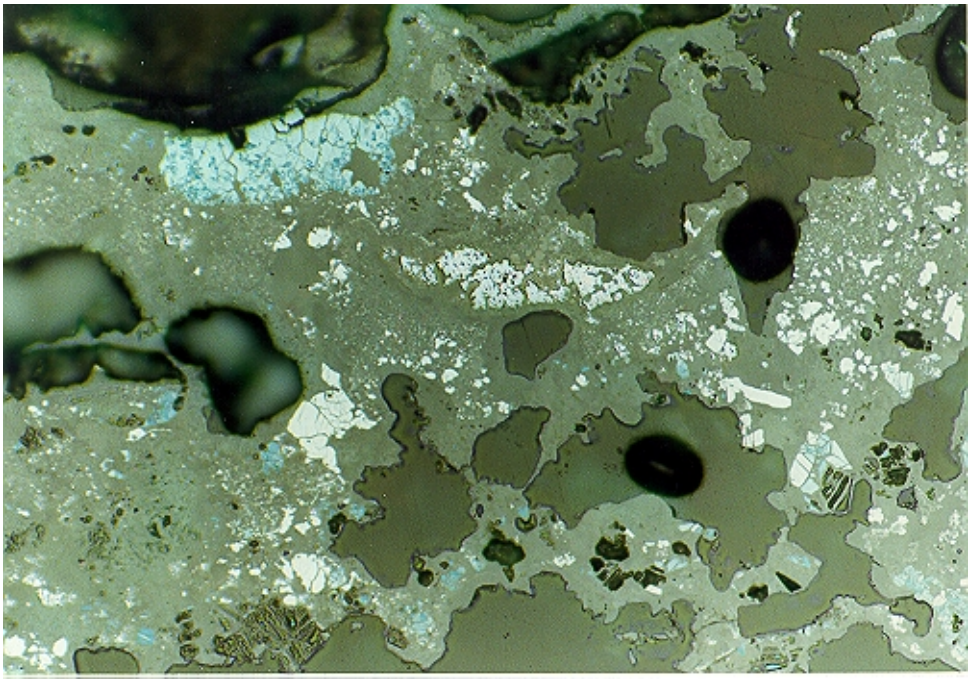


Fig. 3 Photomicrograph of copper sulphides in corrosion overburden.

BF. Width of the image = 0.7 mm.

## Composition:

**AAS:** too corroded for analysis.

**Microanalysis:**

SEM/EDS semi-quantitative analysis has been carried out on the corroded metal (200x); the result is:

| Cu | Sn | Pb | S | Si | Fe | Total |
|---|---|---|---|---|---|---|
| 16.0 | 11.3 | 11.3 | 1.8 | 0.3 | 0.5 | 41.2 |

The poor result which is due to corrosion and porosity suggests that the metal was a high lead bronze.

**Microhardness:** too corroded for measuring.

## CORROSION

**XRD results:** not carried out.

**Metallographic observation:**

The whole piece is totally corroded with some isolated metallic phases left (Fig. 2). Redeposited Cu is seen in cuprite. Different colours of copper sulphides are present in the corrosion overburden (Fig. 3).

**Microanalysis:**

BEI of corroded metal shows that it contains lots of Pb droplets (Fig. 4). The original surfaces are clear in the electron image (Fig. 5). In some areas close to the surface, metallic phases have totally gone (Fig. 5).

## SUMMARY

It is a ternary alloy of Cu-Sn-Pb with a dendritic structure. The composition of the original metal is not estimated, because it is totally corroded. Copper sulphide crystals are present in the corrosion on the surface.

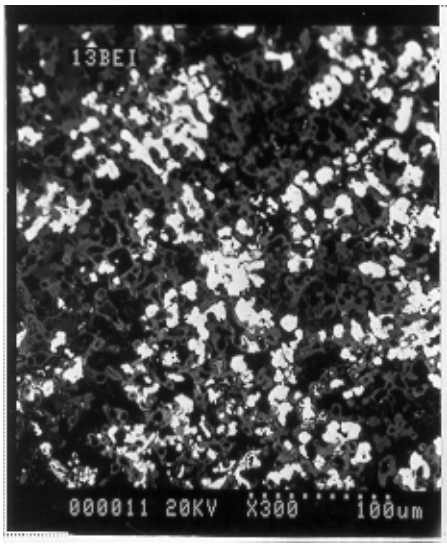



Fig. 4 BEI of corroded metal, showing Pb droplets.

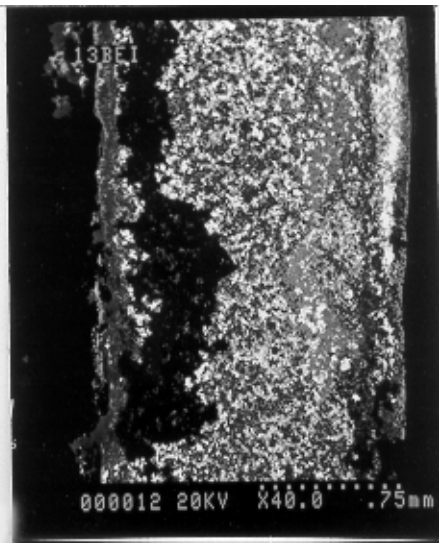



Fig. 5 BEI of the section, showing the original surfaces.

## GENERAL

**Object Number:** M6231:74
**Excavation Date:** 1984
**Origin:** Tianma-Qucun site

**Object:** horse fitting/*luan* bell
**Date:** Early Western Zhou
**Fragment Weight:** 0.3 g
**Fragment size:** 7x4x? mm

**General description:**

There are 2 pieces of small fragments, labelled A, B. Corrosion index is 5 for each of them. Each piece has all sides broken. There are corrosion overburdens on the surface for each, including light green, green, dark green and black corrosion products. No decoration is apparent.

## TECHNICAL STUDIES OF METAL

**Metallographic structure:**

Based on the flat shapes of the fragments, it seems that they (Fig. A, 1; Fig. B, 1) were from the stand. Both are of cast dendritic structure. One surface of each piece is broken, therefore, the original dimensions could not be estimated.

**Composition:**

**AAS:** too corroded for analysis.

**Microanalysis:**

See corrosion section.

**Microhardness:** too corroded for measuring.

## CORROSION

**XRD results:** not carried out.

**Metallographic observation:**

Both pieces are totally corroded, with δ phases remaining in the corroded metals. Copper sulphide has banded shapes in A (Fig. A, 2), while crystals with fractures are in B (Fig. B, 1). The band-shaped sulphides in A could be formed by organic materials, since plenty of fibrous materials are observed in the corrosion overburden

(Fig. A, 3). Black layers are observed in both fragments, it is 50-83 μm thick in A, and 110-220 μm thick in B. The black layer in B is sandwiched between two layers of cuprite (Fig. B, 2).

**Microanalysis:**

EPMA results are as follows. Points are not marked in the accompanying pictures but described in the last column. Bronze disease was not detected by microanalysis. Lead inclusions are not apparent.

| Point | Cu | Ni | Fe | Sn | Pb | As | Zn | Co | S | Cl | total | Description |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 75.26 | 0.00 | 0.05 | 1.05 | 0.16 | 0.00 | 0.00 | 0.00 | 19.81 | 0.06 | 96.39 | A: banded material |
| **2** | 77.69 | 0.00 | 0.01 | 0.03 | 0.00 | 0.00 | 0.00 | 0.00 | 20.90 | 0.00 | 98.63 | A: white sulphide |
| **3** | 65.51 | 0.00 | 0.08 | 0.04 | 0.05 | 0.00 | 0.00 | 0.00 | 24.33 | 0.00 | 90.01 | A: blue sulphide |
| **4** | 65.40 | 0.00 | 0.10 | 0.01 | 0.01 | 0.00 | 0.00 | 0.00 | 16.74 | 0.00 | 82.26 | A: light blue sulphide |
| **5** | 31.10 | 0.00 | 1.89 | 44.39 | 0.48 | 0.00 | 0.00 | 0.01 | 4.56 | 0.02 | 82.45 | B: black layer |
| **6** | 56.21 | 0.01 | 0.02 | 0.08 | 0.00 | 0.00 | 0.00 | 0.00 | 0.02 | 0.00 | 56.34 | B: green corrosion |

EPMA lines across corrosion area of B was carried out, the results are plotted in Fig. B, 3. From outmost corrosion inwards the sequence of corrosion products represents: mixtures of copper sulphide and carbonate, carbonate and then a black layer. There is a correlation between Fe and Sn, with Fe increasing with Sn. Hg was detected in 3 out of 21 points, with concentration of 0.90, 4.04, and 0.96% respectively. All these 3 points are in the outer corrosion layer rather than in the black layer. It suggests that Hg is the result of contamination of the burial environment.

**SUMMARY**

Technical study supports the conclusion that these 2 pieces were from different parts of the same object. Both are a binary alloy of Cu-Sn with a dendritic structure. Both pieces are totally corroded, therefore the original composition could not be estimated. Copper sulphide is present in the corrosion for both pieces. There is a black layer on piece B.

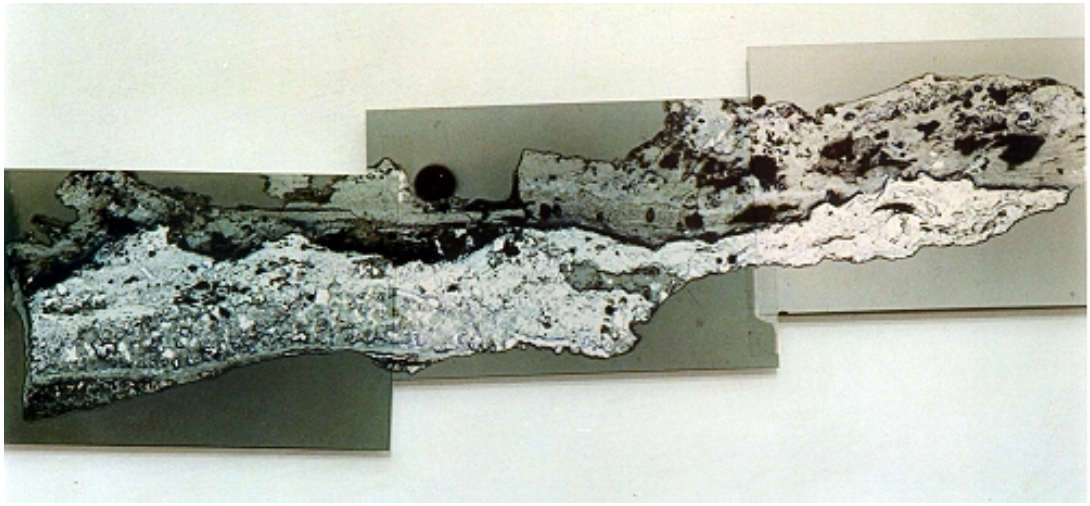


Fig. A, 1 The whole metallographic section.

BF. Width of the image = 8mm.

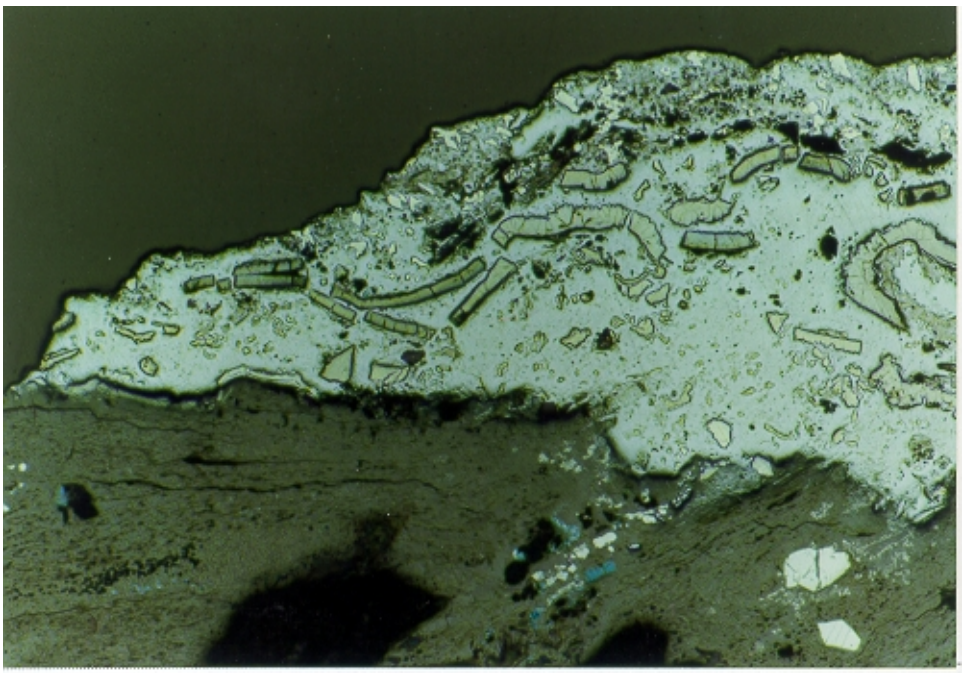


Fig. A, 2 Photomicrograph of copper sulphide bands in the corroded metal.

BF. Width of the image = 1.1 mm.

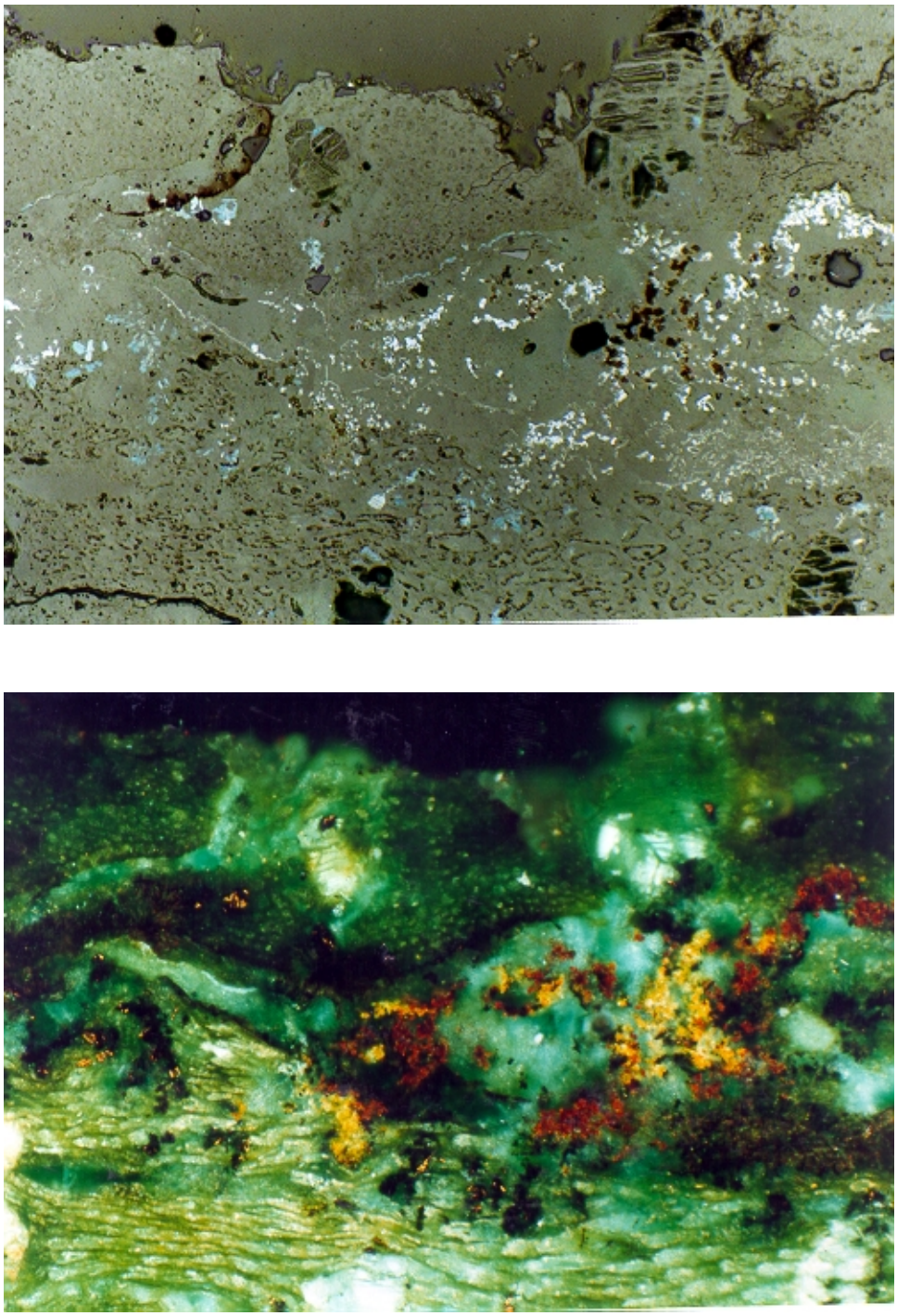


Fig. A, 3 Photomicrograph of fibrous materials in the corrosion overburden.

Top: BF.  Bottom: C/P.

Width of the image = 0.7 mm.

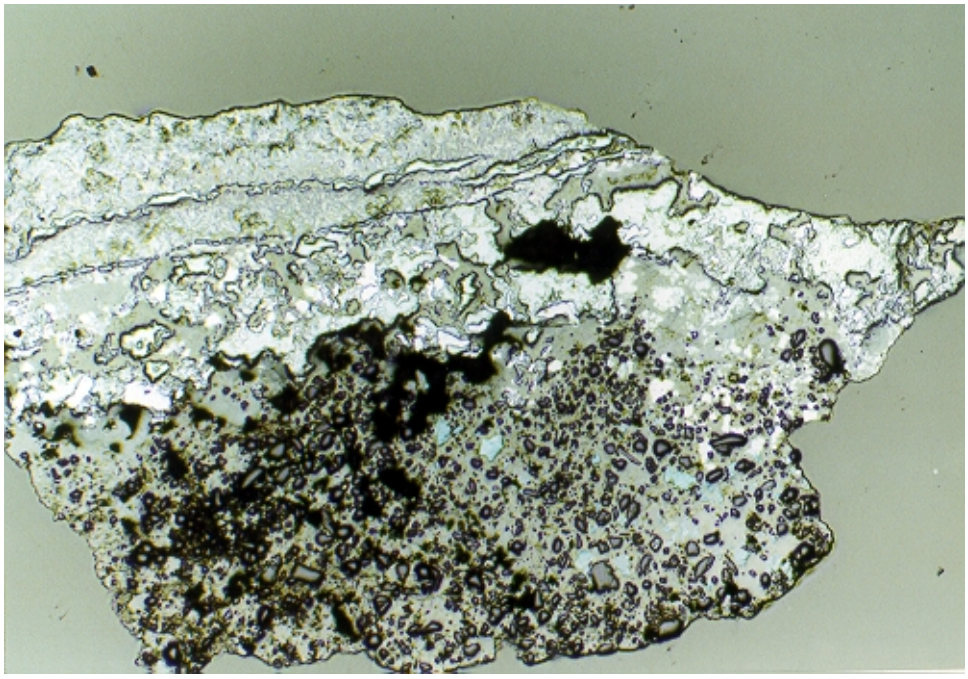


Fig. B, 1 The metallographic section.
BF. Width of the image = 2.8 mm.

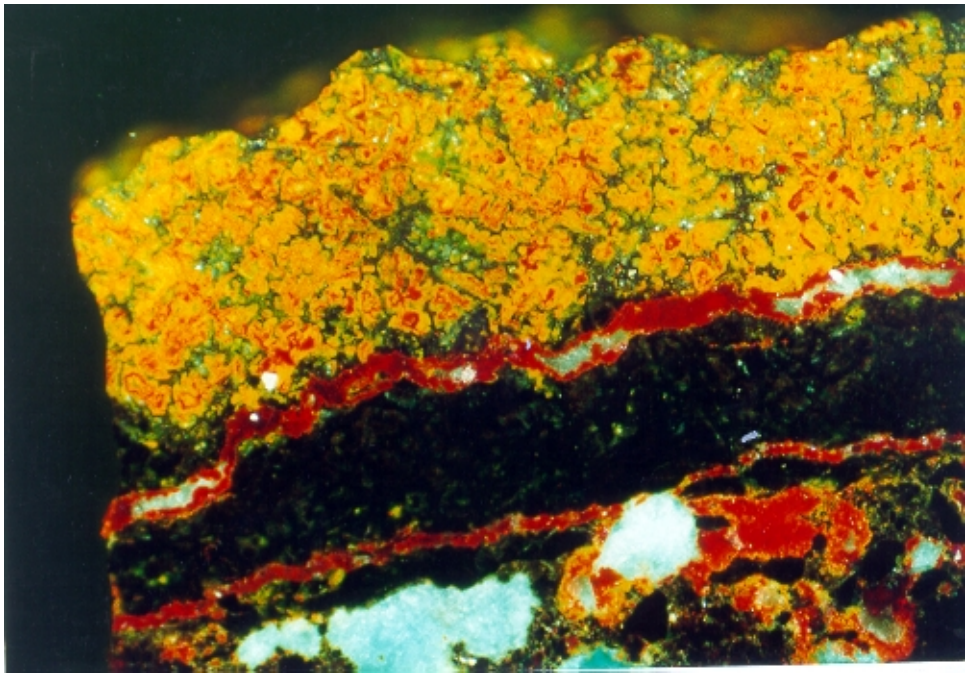


Fig. B, 2 Photomicrograph of the black layer on the surface.
C/P. Width of the image = 0.9 mm.

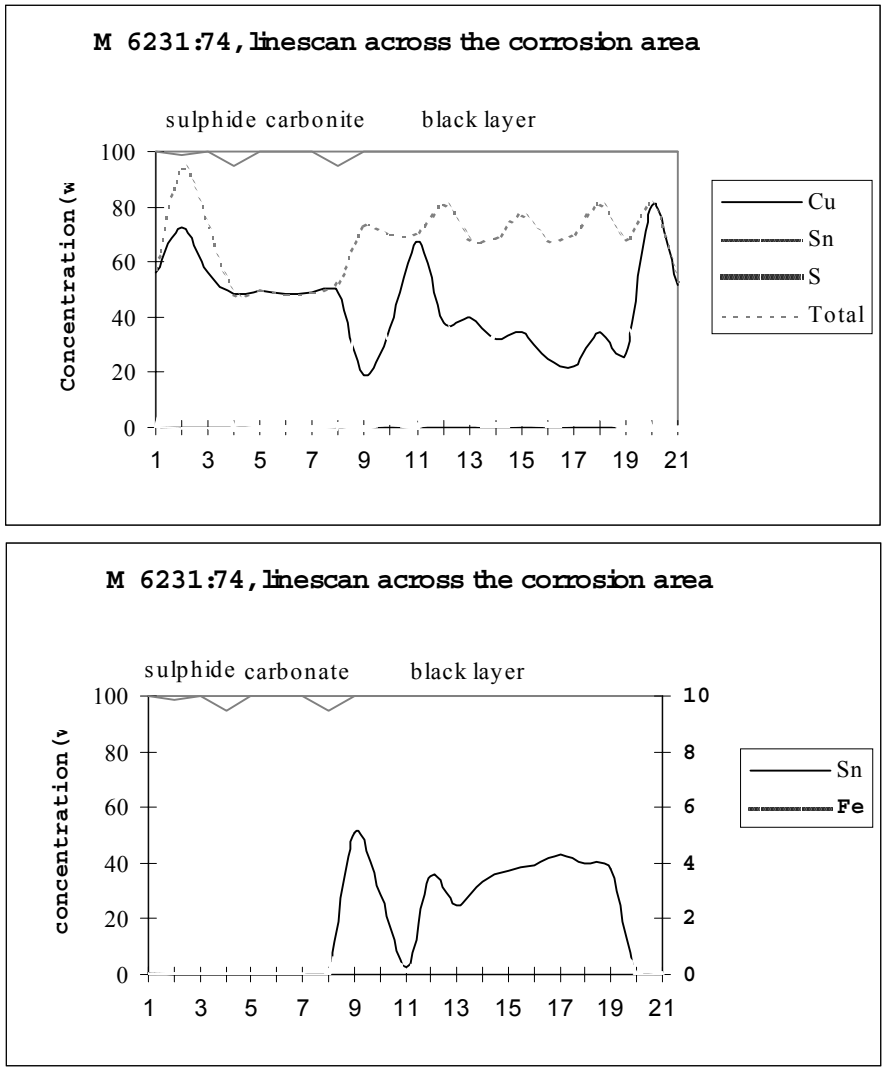



Fig. B, 3 EPMA linescan across the corrosion layers.

## GENERAL

**Object Number:** M6231:79
**Excavation Date:** 1984
**Origin:** Tianma-Qucun site

**Object:** weapon/*ge* spear
**Date:** Early Western Zhou
**Fragment Weight:** 0.1 g
**Fragment size:** 4x3x3.5 mm

**General description:**

This fragment has all sides broken. Corrosion index is 5. There is a corrosion overburden on the surface, including light green, green, red and black corrosion products and soil. No decoration is apparent. It was probably from the body rather than an edge based on its thickness. (Fig. 1)

## TECHNICAL STUDIES OF METAL

**Metallographic structure:**

A section cut through the full length of the fragment was taken for metallographic observation. The original surfaces can still be seen but disrupted. The estimated thickness is 3.5 mm as measured in the metallographic section. It has a dendritic structure (Fig. 2). The estimated dendritic arm spacing is 0.059 mm.

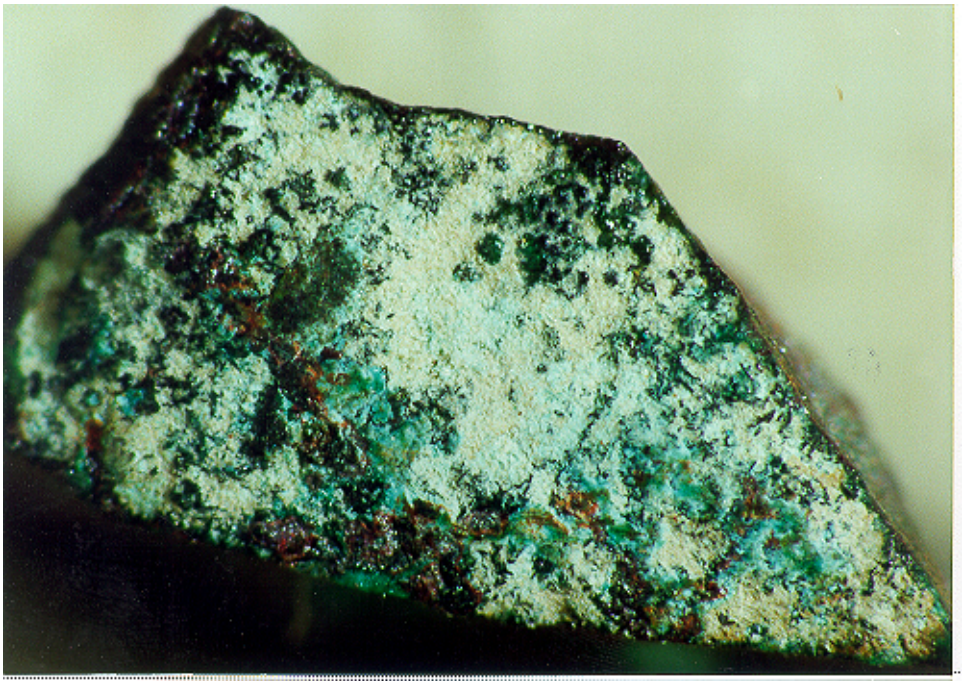


Fig. 1 General view of the fragment.
Width of the image = 4.5 mm.

**Composition:**

**AAS:** too corroded for analysis.

**Microanalysis:**

SEM/EDS semi-quantitative analysis on the corroded metal (200x) shows it was a binary alloy of Cu-Sn.

| Cu | Sn | Fe | Si | Total |
|---|---|---|---|---|
| 37.8 | 19.2 | 0.9 | 0.4 | 58.3 |

**Microhardness:** too corroded for measuring.

## CORROSION

**XRD results:**

Light green corrosion products: brochantite, langite.

**Metallographic observation:**

The whole piece is totally corroded; no metallic phase has been preserved at all. Only a pseudomorphic dendritic structure can be seen. There are black layers on both surfaces (Fig. 2).

**Microanalysis:**

EPMA spot analysis was carried out on the corroded metal and corrosion on the surface, the results are as follows (Fig. 3):

| Point | Cu | Fe | Sn | Pb | S | Cl | Ag | Bi | As | Total | Description |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 35.75 | 2.08 | 31.32 | 0.04 | 6.56 | 0.05 | 0.96 | 0.00 | 0.00 | 76.75 | Black layer |
| **2** | 79.11 | 0.03 | 0.03 | 0.03 | 2.09 | 0.04 | 0.04 | 0.00 | 3.17 | 84.54 | Cuprite |
| **3** | 46.16 | 5.02 | 17.59 | 0.00 | 1.40 | 0.01 | 0.59 | 0.04 | 0.00 | 80.79 | Black layer |
| **4** | 54.25 | 1.43 | 17.46 | 0.18 | 0.23 | 0.08 | 0.01 | 0.11 | 1.59 | 75.33 | Corroded α |
| **5** | 81.11 | 0.03 | 0.10 | 0.04 | 0.00 | 0.16 | 0.00 | 0.00 | 0.00 | 81.45 | Cuprite |
| **6** | 44.90 | 1.33 | 23.11 | 0.14 | 0.14 | 0.10 | 0.01 | 0.00 | 2.77 | 72.49 | Corroded eutectoid |
| **7** | 17.58 | 1.99 | 35.08 | 0.03 | 0.24 | 0.04 | 0.00 | 0.03 | 3.99 | 58.97 | Corroded α |

## SUMMARY

It is a binary alloy of Cu-Sn with no lead inclusions based on SEM/EDS and EPMA analysis. The original composition is not estimated, because it is totally corroded. It

has a dendritic structure. A black layer is present on each of the original surfaces. There is remarkable amount of As in the corrosion.

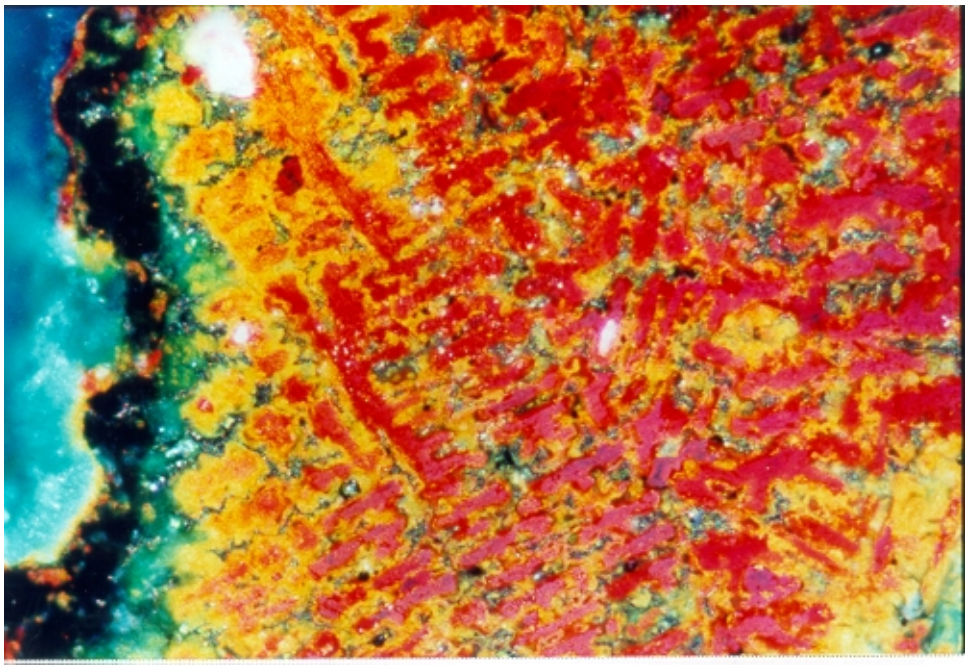


Fig. 2 Photomicrograph of the black layer on the surface.
C/P. Width of the image = 0.5 mm.

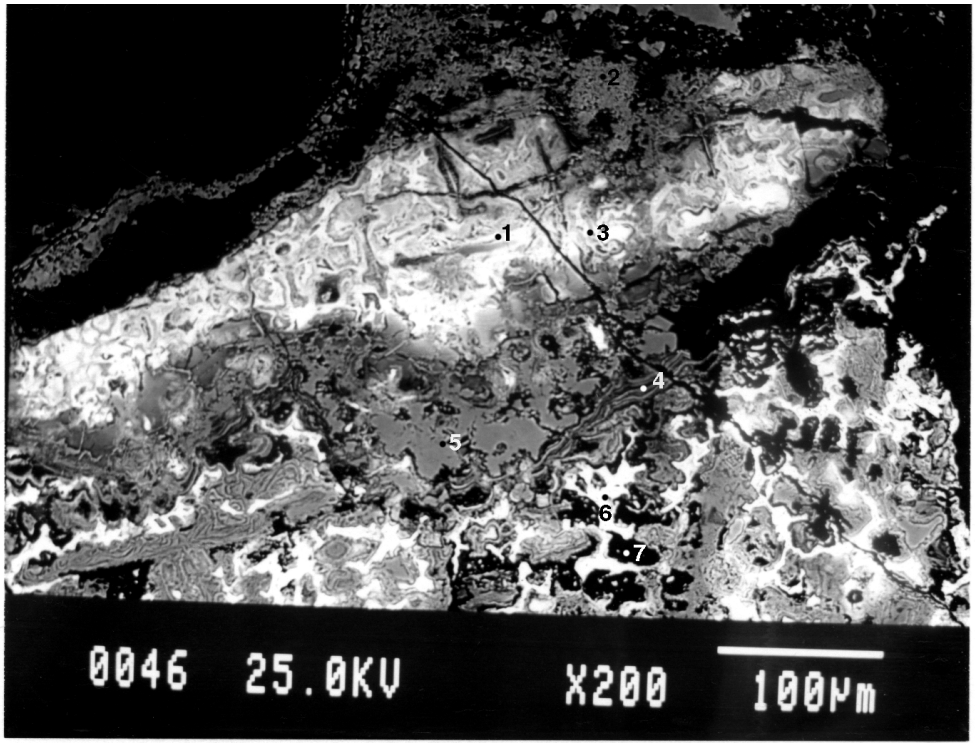



Fig. 3 BEI of corroded metal, showing EPMA points.

## GENERAL

**Object Number:** M6195:4

**Object:** horse fitting/nose ornament (Fig.1 )

**Excavation Date:** 1984

**Date:** Early Western Zhou

**Origin:** Tianma-Qucun site

**Fragment Weight:** 0.9 g

**Fragment size:** 12x8x0.9 mm

**General description:**

This fragment has all sides broken. Corrosion index is 5. There is a corrosion overburden and soil on the surface, including light green, green and black corrosion products. No decoration is apparent.

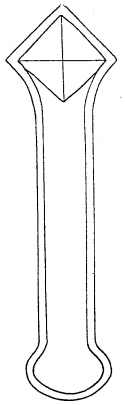


Fig. 1 The object

## TECHNICAL STUDIES OF METAL

**Metallographic structure:**

A section cut through the full length of the fragment was taken for metallographic observation. The curved shape of the section indicates that this fragment was from an end rather than the middle of the object. The original surfaces are disrupted by corrosion. The estimated thickness is about 0.9 mm as measured in the metallographic section. It has a dendritic structure (Fig. 2).

**Composition:**

**AAS:** too corroded for analysis.

**Microanalysis:**

SEM/EDS semi-quantitative analysis was carried out on the corroded metal (200x), the result only shows that it is a ternary alloy of Cu-Sn-Pb. The original composition is not estimated because of corrosion.

| Cu | Sn | Pb | As | Si | Total |
|---|---|---|---|---|---|
| 28.3 | 20.5 | 19.0 | 1.0 | 0.5 | 69.3 |

**Microhardness:** too corroded for measuring.

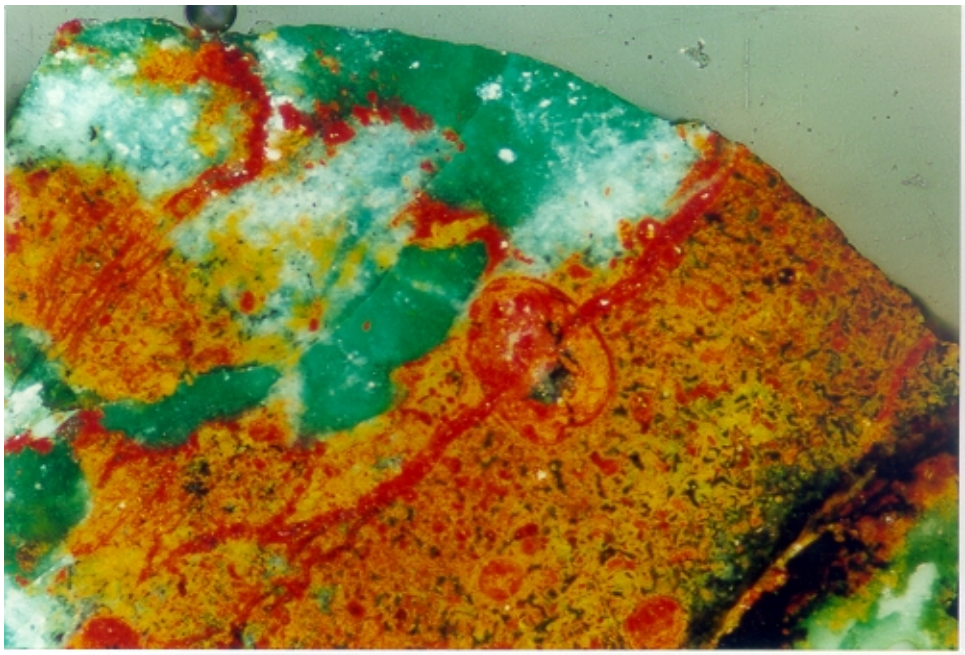


Fig. 2 Photomicrograph of corroded metal.
The green materials on the left upper corner is atacamite, confirmed by EPMA and XRD.
C/P. Width of the image = 1mm.

## CORROSION

### XRD results:

Surface sample: malachite, cuprite, atacamite.

**Metallographic observation:**

The whole piece is totally corroded with some isolated δ phases being seen. α phase is almost totally gone. The outer (convex) surface is disrupted and expanded by green corrosion products, which were suspected to be bronze disease (Fig. 2). There is almost no corrosion overburden developed on this surface. On the inner (concave) surface, corrosion overburden is up to 1.6 mm thick, comprised of interlaced corrosion of green, black and red materials. Redeposited Cu is seen in cuprite. Different colours of copper sulphides are seen in the corrosion overburden.

**Microanalysis:**

EPMA was carried out on the corroded metal and corrosion overburden (Figs. 3 & 4), the results show that the outer surface has been disrupted by bronze disease.

| Point | Description |
|---|---|
| **1, 2** | Chloride |
| **3, 4** | Corroded metal |
| **5, 6, 7** | Disrupted surface by chloride |
| **8** | Lead droplet |
| **9, 10** | Corrosion overburden on the inner surface |

| Point | Cu | Fe | Sn | Pb | As | Ag | S | Cl | Bi | total |
|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 50.44 | 0.00 | 0.00 | 0.17 | 0.00 | 0.05 | 0.03 | 17.56 | 0.11 | 68.38 |
| **2** | 36.69 | 0.01 | 0.00 | 0.75 | 0.00 | 0.00 | 0.18 | 17.90 | 0.02 | 55.54 |
| **3** | 4.52 | 0.23 | 14.28 | 32.41 | 0.00 | 0.00 | 0.37 | 0.30 | 0.00 | 52.10 |
| **4** | 16.93 | 0.31 | 31.95 | 18.49 | 1.41 | 0.00 | 0.04 | 1.73 | 0.18 | 71.02 |
| **5** | 46.76 | 0.00 | 0.12 | 1.34 | 0.00 | 0.03 | 0.01 | 2.54 | 0.08 | 50.88 |
| **6** | 52.44 | 0.00 | 0.00 | 0.40 | 0.00 | 0.09 | 0.03 | 12.66 | 0.00 | 65.63 |
| **7** | 49.81 | 0.00 | 0.02 | 1.45 | 1.00 | 0.04 | 0.03 | 4.39 | 0.00 | 56.74 |
| **8** | 0.33 | 0.05 | 0.05 | 89.81 | 0.00 | 0.00 | 0.00 | 0.52 | 0.00 | 90.75 |
| **9** | 44.66 | 0.15 | 0.06 | 2.49 | 0.00 | 0.00 | 0.26 | 0.02 | 0.00 | 47.62 |
| **10** | 31.77 | 6.70 | 0.09 | 11.72 | 7.56 | 0.00 | 0.24 | 0.11 | 0.00 | 58.18 |

## SUMMARY

It is a ternary alloy of Cu-Sn-Pb with high Pb content. It has a dendritic structure. The original composition is not estimated, because it is totally corroded. The outer surface has been attacked by chloride. Redeposited Cu and copper sulphide are present in the corrosion.

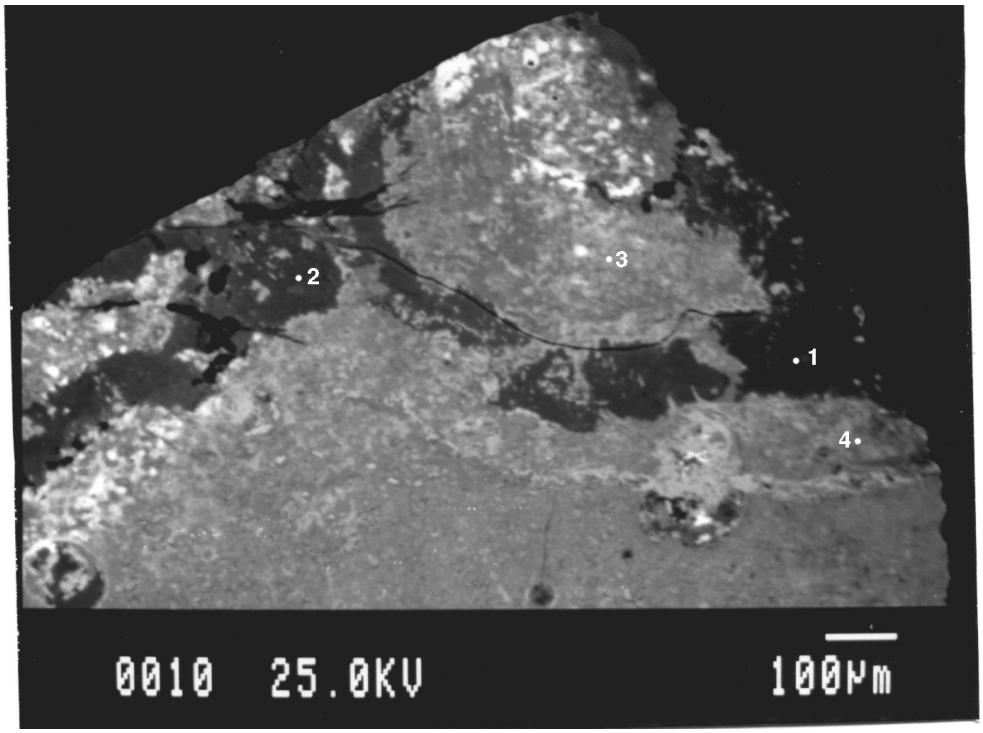



Fig. 3 BEI of corroded metal, corresponding to Fig. 2 (rotated about 90°), showing EPMA points.

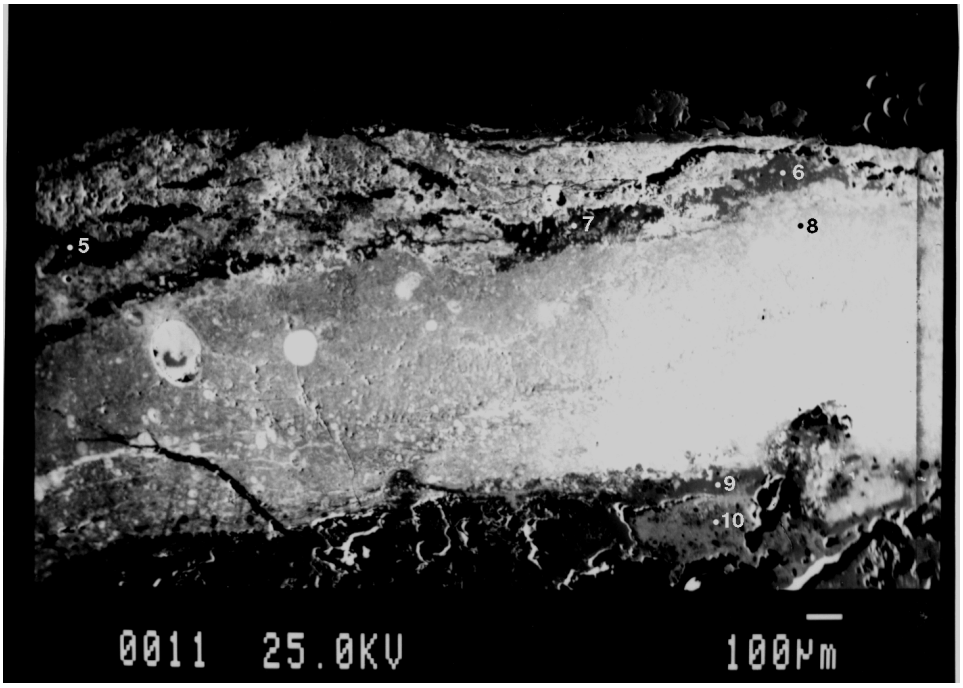



Fig. 4 SEI of the metallographic section, showing EPMA points.

## GENERAL

**Object Number:** M6195:18

**Object:** horse fitting/ harness (Fig. 1)

**Excavation Date:** 1984

**Date:** Early Western Zhou

**Origin:** Tianma-Qucun site

**Fragment Weight:** 1.0 g

**Fragment size:** 8x6x4 mm

**General description:**

This fragment has all sides broken. Corrosion index is 5. There is a corrosion overburden on the surface. No decoration is apparent (Fig. 2). The fragment was probably from the body of the object based on its shape.

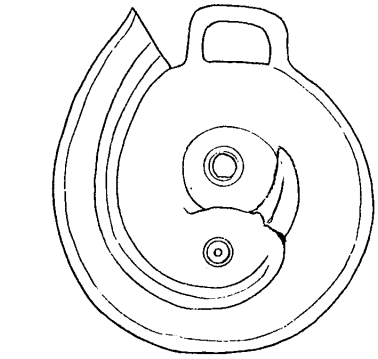


Fig. 1 The object

Fig. 2 General view of the fragment. Width of the image = 11 mm.

## TECHNICAL STUDIES OF METAL

### Metallographic structure:

The whole piece was mounted for metallographic section. The original dimension is well preserved although it is totally corroded. The estimated thickness is about 4 mm as measured in the metallographic section. It seems like dendritic structure based on photomicrograph (Fig. 3) and electron image (Fig. 4) of the corroded metal.

### Composition:

**AAS:** too corroded for analysis.

**Microanalysis:**

SEM semi-quantitative analysis was carried out on the corroded metal (Fig. 4), the results show that it is a binary alloy of Cu-Sn.

Point 1:

| Cu | Sn | Fe | Si | Total |
|---|---|---|---|---|
| 61.6 | 13.5 | 0.7 | 0.4 | 72.2 |

Point 2:

| Cu | Sn | Fe | As | S | Si | Total |
|---|---|---|---|---|---|---|
| 49.9 | 12.6 | 1.3 | 1.7 | 2.8 | 0.3 | 68.5 |

Whole area of Fig. 4:

| Cu | Sn | Fe | S | Cl | Total |
|---|---|---|---|---|---|
| 68.9 | 5.7 | 0.4 | 0.5 | 0.2 | 75.7 |

**Microhardness:** too corroded for measuring.

## CORROSION

**XRD results:** not carried out.

### Metallographic observation:

The whole piece is totally corroded with some isolated α phases being preserved (Fig. 3). Redeposited Cu is present in cuprite on the surface. Different colours of copper sulphides are observed in the corrosion overburden.

**Microanalysis:** not carried out

## SUMMARY

It is a binary alloy of Cu-Sn with a dendritic structure. The original alloy composition is not estimated because it is totally corroded. Both redeposited Cu and sulphide are present in the corrosion.

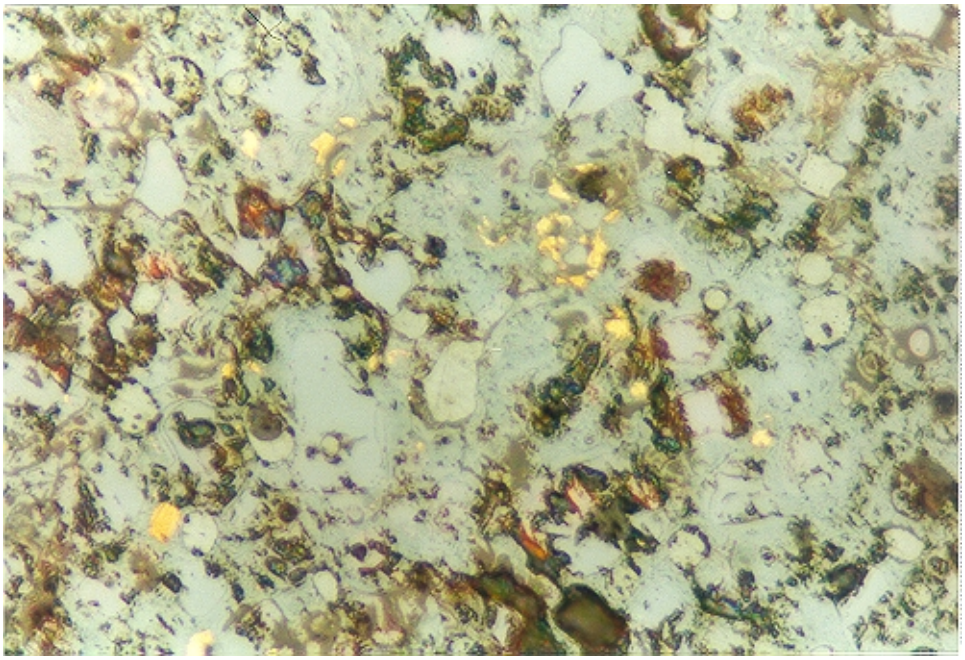


Fig. 3 Microstructure of the corroded metal.
BF. Width of the image = 0.2 mm.

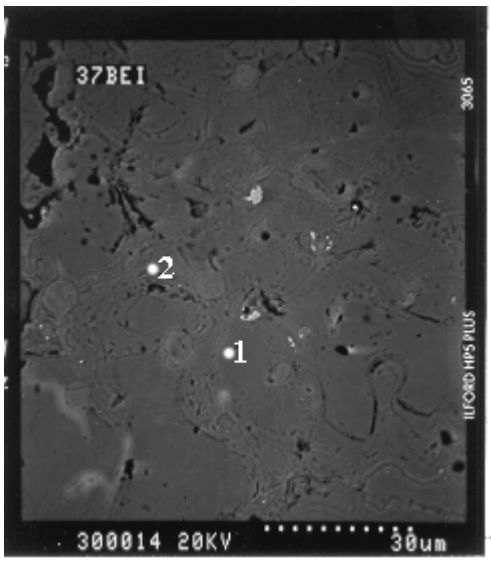



Fig. 4 BEI of corroded metal, showing pseudomorphic dendritic structure and SEM/EDS points.

## GENERAL

**Object Number:** M6195:20
**Excavation Date:** 1984
**Origin:** Tianma-Qucun site

**Object:** vessel/*ding* (Fig. 1)
**Date:** Early Western Zhou
**Fragment Weight:** 0.8 g
**Fragment size:** 12x10x(0.7-1.0) mm

**General description:**

This fragment was from a leg of the object. It has all sides broken. Corrosion index is 5. There is a corrosion overburden and soil on the surface, including light green, grey, and black corrosion products (Fig. 2). The colour of the cross section, pale green, seems different from an ordinary bronze (Fig. 3). No decoration is apparent.

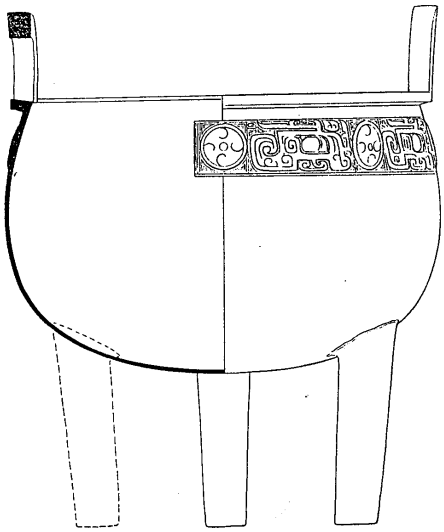


Fig. 1 The object

## TECHNICAL STUDIES OF METAL

**Metallographic structure:**

The smaller piece on the right of Fig. 2 was taken for metallographic section. The original surfaces are well preserved although the metal is totally corroded. The estimated thickness is 0.7-1.0 mm as measured in the metallographic section. Its structure is not evident.

**Composition:**

**AAS:** too corroded for analysis.

**Microanalysis:**

SEM/EDS semi-quantitative analysis was carried out on different areas of the corroded metal; the results are shown below:

Area 1, the thinner end (300x):

| Cu | Sn | Pb | Fe | As | Si | P | Ca | Total |
|---|---|---|---|---|---|---|---|---|
| 26.9 | 16.5 | 17.1 | 2.2 | 0.7 | 0.4 | 0.5 | 0.1 | 64.4 |

Area 2, the middle (300x):

| Cu | Sn | Pb | Fe | As | Si | Ca | Total |
|---|---|---|---|---|---|---|---|
| 6.2 | 23.2 | 8.8 | 0.7 | 0.9 | 0.3 | 0.4 | 40.5 |

Area 3, the wider end (300x):

| Cu | Sn | Pb | Fe | As | Si | Total |
|---|---|---|---|---|---|---|
| 6.0 | 26.2 | 11.9 | 0.6 | 0.8 | 0.3 | 45.8 |

It seems that this is a ternary alloy of Cu-Sn-Pb with relatively high Pb content.

**Microhardness:** too corroded for measuring.

Fig. 2 General view of the fragment.
Width of the image = 14 mm.

Fig. 3 View of cross section of the fragment.
Width of the image = 14 mm.

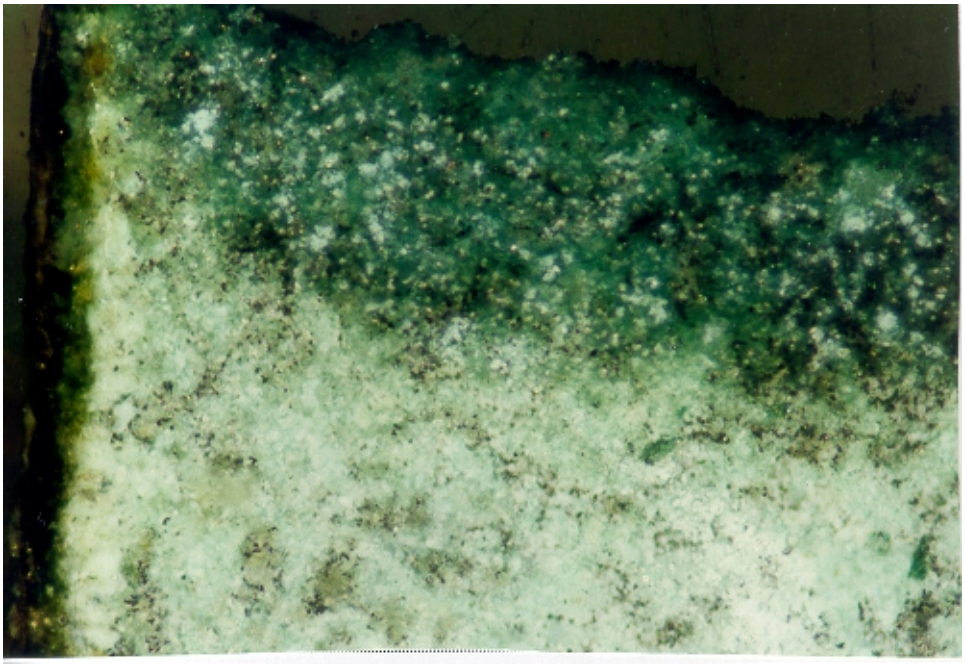


Fig. 4 Photomicrograph of corroded metal at the smaller end.
C/P. Width of the image = 0.9 mm.

## CORROSION

### XRD results:

Surface sample: cerussite.

### Metallographic observation:

Unlike other bronzes, which appeared reddish or yellowish in colour by converting to cuprite and cassiterite during the corrosion process, this piece appeared light green after corrosion (Fig. 4). Cuprite is only seen at one end where redeposited Cu is also present.

### Microanalysis:

EPMA was carried out on the corroded metal and corrosion overburden, the results are as follow (Figs. 5 & 6):

| Point | Description |
|---|---|
| **1 - 3** | Light green part (Fig. 4) of the corroded metal |
| **4 - 8** | Dark green part (Fig. 4) of the corroded metal |
| **9 - 12** | Corrosion overburden |

| Point | Cu | Fe | Sn | Pb | As | Hg | Sb | Ag | S | Cl | Bi | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 1.50 | 0.29 | 2.32 | 64.94 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.04 | 0.30 | 69.48 |
| **2** | 31.06 | 0.19 | 18.86 | 18.89 | 0.00 | 0.00 | 0.00 | 0.25 | 0.00 | 0.01 | 0.10 | 69.36 |
| **3** | 1.54 | 0.28 | 5.03 | 65.37 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.08 | 0.00 | 72.29 |
| **4** | 1.26 | 0.57 | 16.11 | 54.71 | 0.00 | 0.00 | 0.00 | 0.02 | 0.00 | 0.06 | 0.03 | 72.75 |
| **5** | 0.93 | 0.21 | 1.37 | 65.15 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.04 | 0.03 | 67.74 |
| **6** | 2.59 | 1.10 | 19.22 | 49.11 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.14 | 0.02 | 72.17 |
| **7** | 5.77 | 2.40 | 34.66 | 13.88 | 0.00 | 0.00 | 0.00 | 0.03 | 0.14 | 0.21 | 0.13 | 57.21 |
| **8** | 6.57 | 1.77 | 34.76 | 28.93 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.16 | 0.24 | 72.43 |
| **9** | 0.53 | 0.07 | 0.04 | 89.12 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 2.16 | 0.59 | 92.50 |
| **10** | 0.58 | 0.90 | 0.02 | 33.91 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.97 | 28.95 | 65.34 |
| **11** | 1.26 | 1.03 | 0.00 | 65.71 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.20 | 0.78 | 68.98 |
| **12** | 0.40 | 0.22 | 0.00 | 85.67 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.19 | 0.00 | 86.48 |

## SUMMARY

It is a ternary alloy of Cu-Sn-Pb with high Pb content. The original composition is not estimated, because it is totally corroded. Its structure is not identified. Redeposited Cu is present.

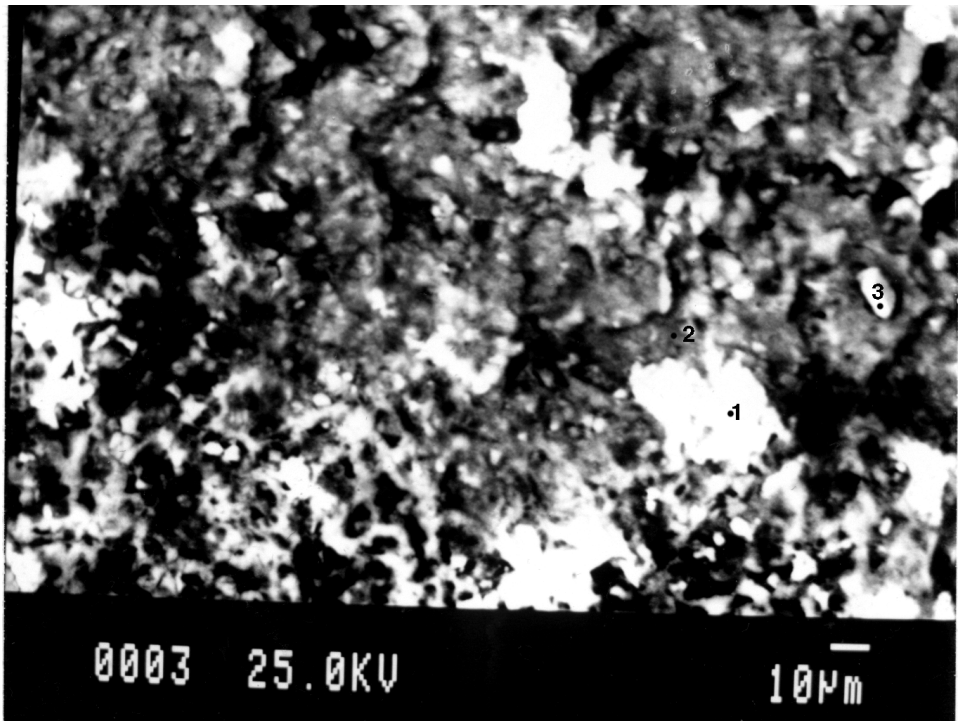



Fig. 5 BEI of corroded metal, showing EPMA points.

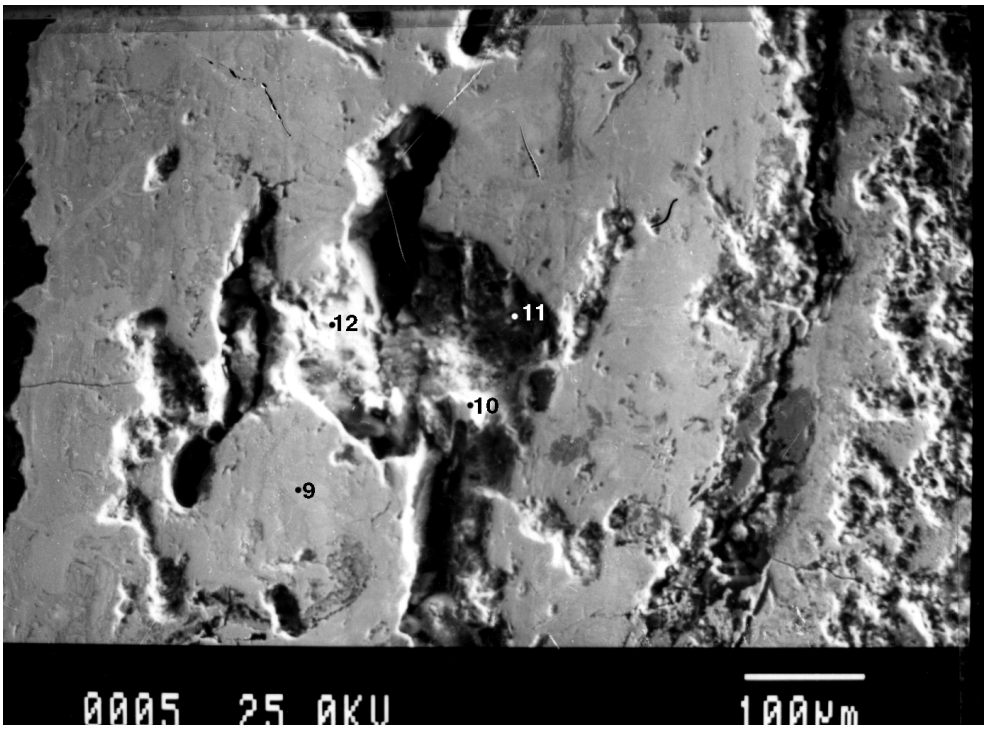



Fig. 6 SEI of corrosion overburden, showing EPMA points.

## GENERAL

**Object Number:** M6195:41
**Excavation Date:** 1984
**Origin:** Tianma-Qucun site

**Object:** horse fitting/*luan* bell
**Date:** Early Western Zhou
**Fragment Weight:** 0.1 g
**Fragment size:** 4x3x3.2 mm

**General description:**

This small fragment has all sides broken. Corrosion index is 4. There is a corrosion overburden on the surface, including light green, green, and black corrosion products. No decoration is apparent.

## TECHNICAL STUDIES OF METAL

**Metallographic structure:**

The whole piece was mounted for metallographic section. The original surfaces can be seen. The estimated thickness is 3.2 mm as measured in the metallographic section. It has a dendritic structure; α cores and casting voids are present (Fig. 1). The estimated dendritic arm spacing is 0.062 mm.

**Composition:**

**AAS:** too corroded for analysis.

**Microanalysis:**

SEM/EDS semi-quantitative analysis was carried out on the metal, the results show that it is a binary alloy of Cu-Sn.

| Cu | Sn | Total |
|---|---|---|
| 85.2 | 14.8 | 100.0 |

**Microhardness:** 121Hv

## CORROSION

**XRD results:** not carried out.

**Metallographic observation:**

Most of the section is corroded with a small area of intact metal being preserved. Some α phases are preserved in the corroded metal (Fig. 2); while δ phases are present on most areas of the surface.

Corrosion overburden is comprised of malachite, azurite, cuprite and copper sulphide based on their characteristic colours in the metallographic section.

**Microanalysis:**

EPMA was carried out on the metal (Fig. 1), and on corrosion overburden from the outwards (point 8-11); the results are as follows. Bronze disease was not detected.

| Point | Description |
|---|---|
| **1, 2, 3, 6, 7** | α phase |
| **4, 5** | Eutectoid |
| **5, 6, 7** | Disrupted surface by chloride |
| **8 - 11** | Corrosion overburden |

| Point | Cu | Fe | Pb | As | S | Cl | Ag | Sb | Bi | Hg | Si | P | Al | Sn | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 83.40 | 0.13 | 0.10 | 0.00 | 0.05 | 0.00 | 0.04 | 0.00 | 0.05 | 0.00 | 0.00 | 0.37 | 0.00 | 11.98 | 96.11 |
| **2** | 84.10 | 0.16 | 0.11 | 0.00 | 0.00 | 0.00 | 0.04 | 0.00 | 0.00 | 0.00 | 0.00 | 0.46 | 0.00 | 11.80 | 96.67 |
| **3** | 83.35 | 0.16 | 0.01 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.01 | 0.00 | 0.00 | 0.48 | 0.00 | 13.63 | 97.64 |
| **4** | 81.91 | 0.10 | 0.00 | 0.00 | 0.00 | 0.00 | 0.07 | 0.00 | 0.00 | 0.00 | 0.03 | 0.48 | 0.00 | 16.11 | 98.71 |
| **5** | 82.27 | 0.15 | 0.00 | 0.00 | 0.00 | 0.00 | 0.06 | 0.00 | 0.00 | 0.10 | 0.04 | 0.52 | 0.00 | 16.79 | 99.92 |
| **6** | 86.46 | 0.19 | 0.00 | 0.00 | 0.01 | 0.00 | 0.02 | 0.00 | 0.00 | 0.05 | 0.00 | 0.53 | 0.00 | 12.82 | 100.09 |
| **7** | 89.01 | 0.21 | 0.00 | 0.00 | 0.04 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.49 | 0.00 | 10.26 | 100.02 |
| **8** | 85.60 | 0.20 | 0.14 | 0.00 | 0.15 | 0.00 | 0.03 | 0.00 | 0.00 | 0.05 | 0.00 | 0.54 | 0.00 | 12.84 | 99.54 |
| **9** | 2.87 | 1.68 | 0.00 | 0.00 | 0.12 | 0.21 | 0.00 | 0.00 | 0.08 | 0.00 | 0.47 | 0.40 | 0.37 | 41.98 | 48.98 |
| **10** | 11.80 | 0.16 | 0.13 | 0.59 | 0.15 | 0.20 | 0.02 | 0.00 | 0.11 | 0.05 | 1.36 | 0.90 | 0.20 | 31.58 | 47.26 |
| **11** | 24.67 | 3.53 | 0.12 | 0.00 | 1.58 | 0.38 | 0.00 | 0.00 | 0.10 | 0.06 | 0.69 | 0.60 | 0.00 | 38.60 | 70.32 |

## SUMMARY

It is a binary alloy of Cu-Sn with a dendritic structure. The best estimate of bulk composition determined by SEM/EDS is 85% Cu and 15% Sn. It is deeply corroded, copper sulphide is seen in the corrosion.

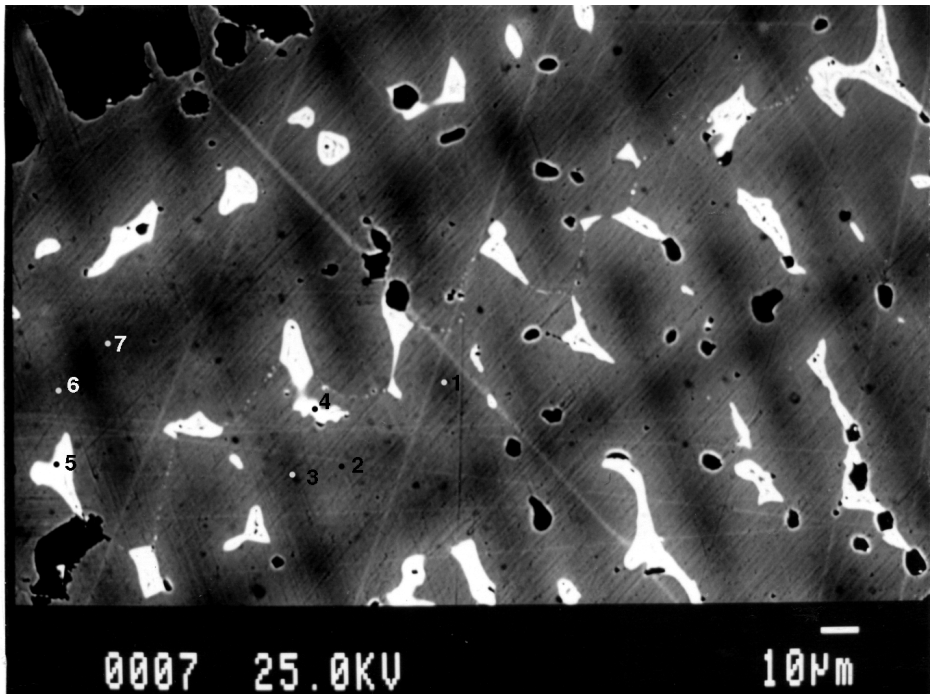



Fig. 1 BEI of metal, showing dendritic microstructure and EPMA points.

Fig. 2 Microstructure of corroded metal, shoing remnant α phase.

BF. Width of the image = 0.7 mm

## GENERAL

**Object Number:** M6195:43
**Excavation Date:** 1984
**Origin:** Tianma-Qucun site

**Object:** horse fitting/*luan* bell
**Date:** Early Western Zhou
**Fragment Weight:** 0.8 g
**Fragment size:** 16x7x(2.5-3.0) mm

**General description:**

This fragment has all sides broken. Corrosion index is 5. There is a very thin corrosion layer on the surface, which comprises green and black materials and soil. Fibrous materials are also seen. No decoration is apparent.

## TECHNICAL STUDIES OF METAL

**Metallographic structure:**

A section cut through the length of the fragment was taken for metallographic observation. The original surfaces can still be seen although the metal is totally corroded. The estimated thickness is 2.5-3.0 mm as measured in the metallographic section. It has a dendritic structure (Fig. 1).

**Composition:**

**AAS:** too corroded for analysis.

**Microanalysis:**

SEM/EDS semi-quantitative analysis shows that it is a ternary alloy of Cu-Sn-Pb.

| Cu | Sn | Pb | Si | Total |
|---|---|---|---|---|
| 17.5 | 23.2 | 14.8 | 0.7 | 56.2 |

**Microhardness:** too corroded for measuring.

## CORROSION

**XRD results:** not carried out.

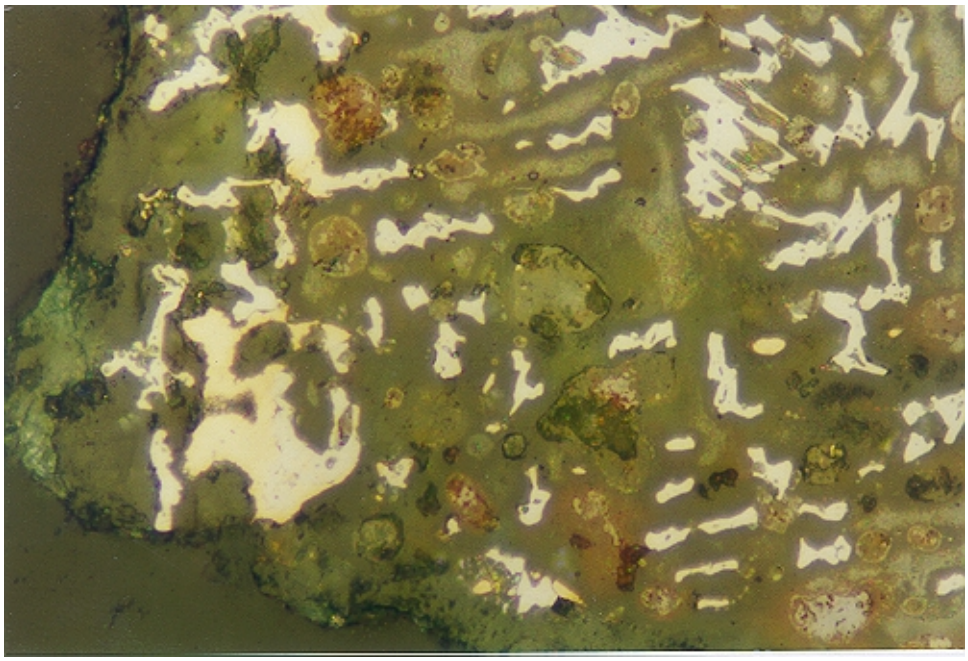


Fig. 1 Photomicrograph of δ-removal corrosion.

BF. Width of the image = 0.2 mm.

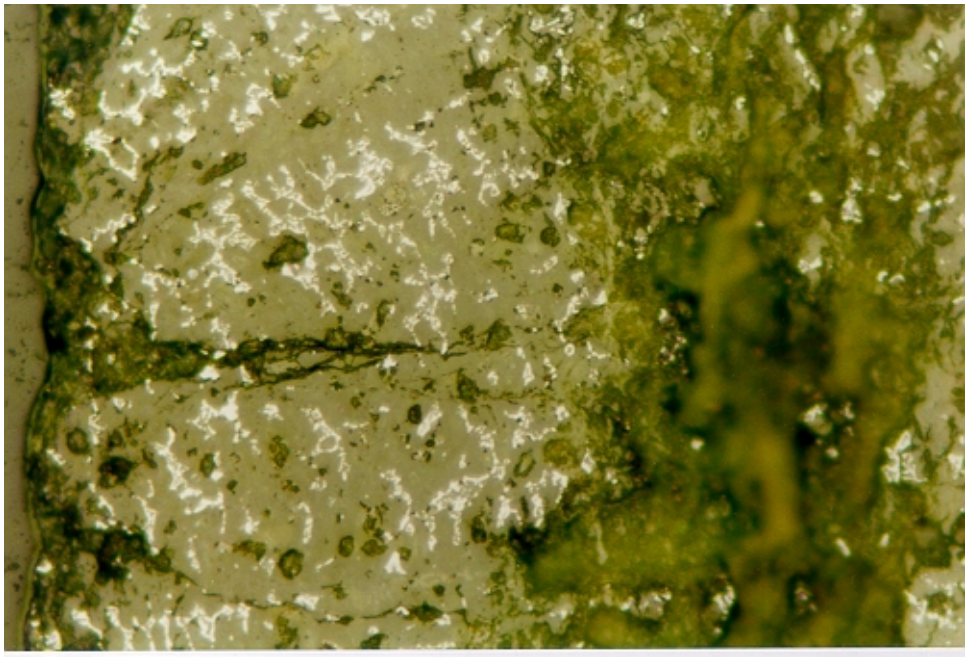


Fig. 2 Photomicrograph of α-removal corrosion.

BF. Width of the image = 0.5 mm.

**Metallographic observation:**

The whole piece is totally corroded with some isolated metallic phases left. δ phases are seen in most areas but α phases are only seen at a corner of the specimen (Figs. 1 & 2). Neither redeposited Cu nor copper sulphide is observed.

**Microanalysis:**

EPMA was carried out on the corroded metal (Fig. 3); the results are as follows:

| point | Cu | Fe | Sn | Pb | As | Hg | Sb | Ag | S | Cl | Bi | total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 9.71 | 0.23 | 16.17 | 11.46 | 0.00 | 0.00 | 0.00 | 0.00 | 0.12 | 0.07 | 0.04 | 37.78 |
| **2** | 7.22 | 2.77 | 35.40 | 4.49 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.04 | 0.00 | 49.92 |
| **3** | 45.12 | 0.04 | 38.32 | 4.16 | 0.00 | 0.00 | 0.00 | 0.04 | 0.00 | 0.02 | 0.00 | 87.69 |
| **4** | 22.71 | 0.05 | 42.73 | 10.82 | 0.00 | 0.00 | 0.00 | 0.00 | 0.02 | 0.05 | 0.07 | 76.43 |
| **5** | 72.15 | 0.01 | 16.92 | 0.23 | 0.00 | 0.00 | 0.00 | 0.03 | 0.03 | 0.00 | 0.00 | 89.37 |
| **6** | 30.55 | 0.09 | 33.65 | 9.19 | 0.00 | 0.00 | 0.00 | 0.00 | 0.09 | 0.14 | 0.03 | 73.74 |
| **7** | 42.31 | 0.07 | 14.06 | 19.19 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.12 | 0.14 | 75.88 |

The results of EPMA indicate that it was a leaded bronze. Chloride was not detected by EPMA.

**SUMMARY**

It is a ternary alloy of Cu-Sn-Pb with a dendritic structure. The original composition is not estimated, because it is totally corroded.

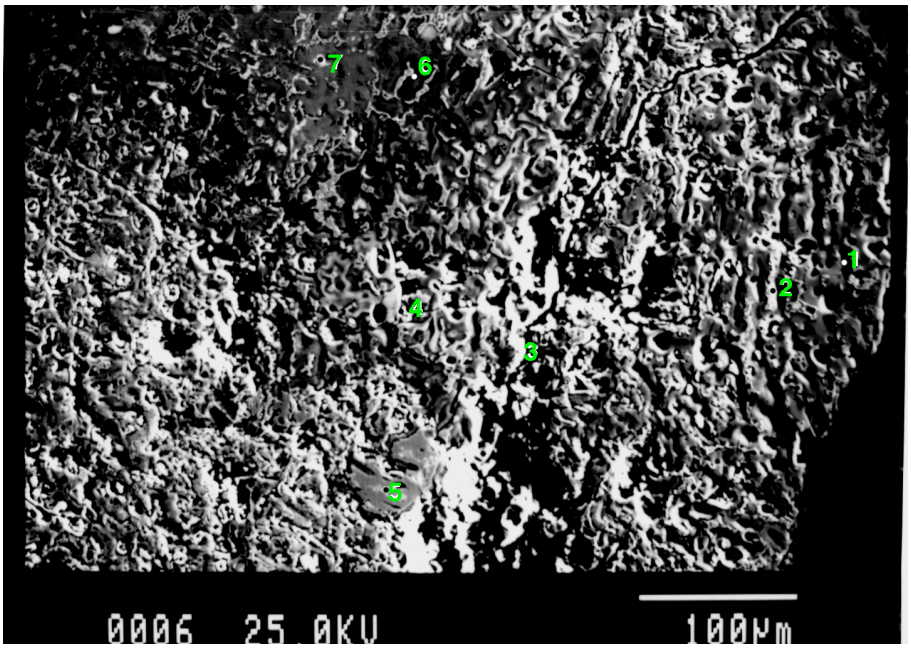



Fig. 3 SEI of corroded metal, showing EPMA points.

## GENERAL

**Object Number:** M6210:8
**Excavation Date:** 1984
**Origin:** Tianma-Qucun site

**Object:** vessel/*zun* (Fig. 1)
**Date:** Early Western Zhou
**Fragment Weight:** 0.3 g
**Fragment size:** 8x8x1.0 mm

**General description:**

This fragment was from a sidewall (either the upper or lower part, because no decoration is apparent). It has all sides broken. Corrosion index is 4. There is a corrosion overburden on the surface, including blue and green corrosion products, fibrous materials and soil. A bit of red corrosion products is also seen on the surface.

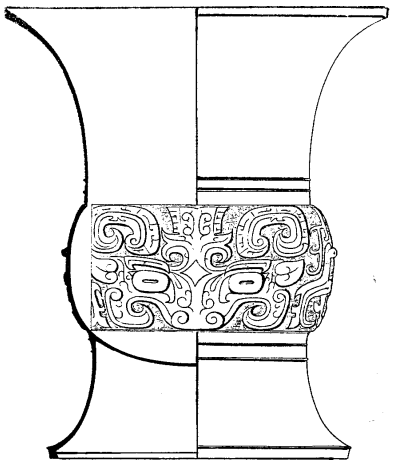


Fig. 1 The object

## TECHNICAL STUDIES OF METAL

**Metallographic structure:**

A section cut through the full width of the fragment was taken for metallographic observation. Original surfaces can be seen. The estimated thickness is 1.0 mm as measured in the metallographic section. It looks like an equi-axed structure (Fig. 2). The estimated grain size is 0.071 mm.

**Composition:**

**AAS:** too corroded for analysis.

**Microanalysis:**

SEM/EDS semi-quantitative analysis was carried out on the least corroded metal (400x). The result shows that it is a binary alloy of Cu-Sn.

| Cu | Sn | Fe | Si | Cl | Total |
|---|---|---|---|---|---|
| 73.2 | 10.0 | 0.3 | 0.1 | 1.3 | 84.9 |

**Microhardness:** 128Hv

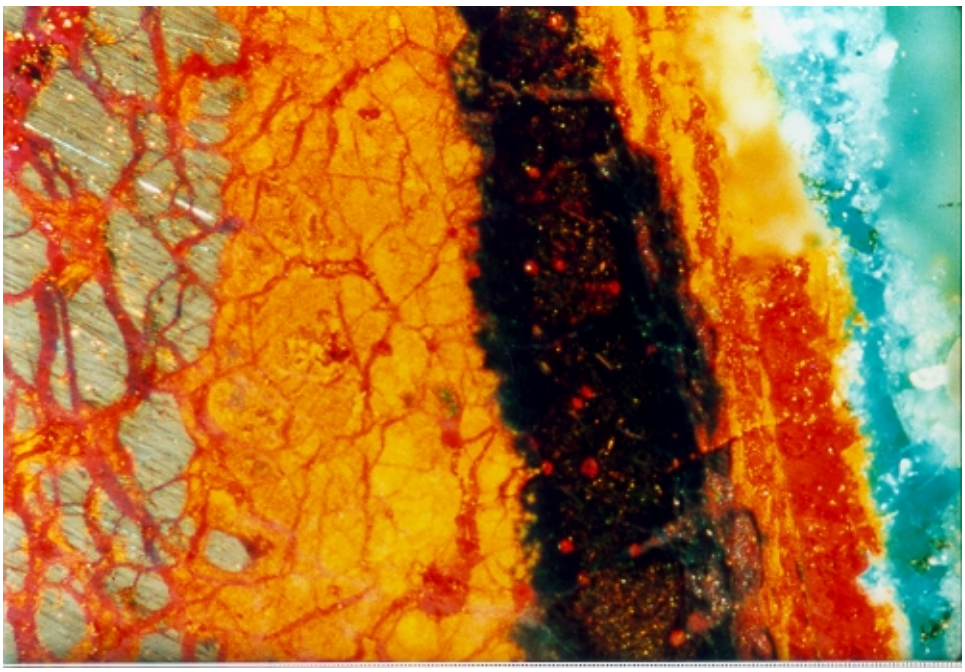


Fig. 2 Photomicrograph of corroded metal, showing a brown – black corrosion layer. C/P. Width of the image = 1 mm.

## CORROSION

**XRD results:** not carried out.

**Metallographic observation:**

It is deeply corroded, with isolated metallic phases left in centre and on one surface (Fig. 3). Intragranular corrosion is observed. Metal is corroded and replaced by cuprite and cassiterite, which mixed to form yellow-reddish colour. There is a black band near a surface (Fig. 3), which appears brown-black in cross polarised light (Fig.

2). Corrosion overburden is mainly comprised of azurite, malachite based on their characteristic colours in the metallographic section.

**Microanalysis:**

EPMA was carried out on the corroded metal (Fig. 3); the results are as follows. The brown – black corrosion layer is rich in Sn.

| Point | Description |
|---|---|
| **1, 2, 3** | α grain in surface |
| **4, 5, 9, 10** | Corrosion under a surface |
| **6, 7, 8** | α grain in center |
| **11, 12** | Intergranular corrosion |
| **13 - 16** | The brown – black corrosion layer under the other surface |
| **17, 18** | Corrosion on the other surface |

| Point | Cu | Fe | Sn | Pb | As | S | Cl | Sb | Bi | Ag | Hg | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 78.25 | 0.35 | 15.43 | 0.03 | 0.00 | 0.02 | 0.03 | 0.00 | 0.00 | 0.03 | 0.00 | 94.13 |
| **2** | 60.12 | 0.28 | 29.19 | 0.10 | 0.00 | 0.02 | 0.00 | 0.00 | 0.20 | 0.04 | 0.00 | 89.94 |
| **3** | 79.81 | 0.32 | 17.85 | 0.18 | 0.00 | 0.19 | 0.02 | 0.00 | 0.06 | 0.05 | 0.10 | 98.57 |
| **4** | 48.24 | 0.54 | 22.54 | 0.00 | 0.00 | 0.20 | 0.54 | 0.00 | 0.15 | 0.00 | 0.00 | 72.20 |
| **5** | 54.58 | 0.49 | 24.06 | 0.00 | 0.00 | 0.23 | 0.33 | 0.00 | 0.00 | 0.00 | 0.00 | 79.69 |
| **6** | 84.11 | 0.32 | 14.51 | 0.03 | 0.00 | 0.00 | 0.00 | 0.00 | 0.03 | 0.04 | 0.00 | 99.04 |
| **7** | 73.88 | 0.33 | 13.82 | 0.02 | 0.00 | 0.01 | 0.00 | 0.00 | 0.19 | 0.03 | 0.00 | 88.27 |
| **8** | 68.68 | 0.31 | 13.02 | 0.00 | 0.00 | 0.02 | 0.00 | 0.00 | 0.11 | 0.01 | 0.00 | 82.14 |
| **9** | 49.35 | 0.34 | 18.83 | 0.08 | 2.05 | 0.16 | 0.11 | 0.00 | 0.00 | 0.01 | 0.00 | 70.91 |
| **10** | 60.78 | 0.45 | 21.46 | 0.08 | 0.00 | 0.16 | 0.22 | 0.00 | 0.08 | 0.00 | 0.00 | 83.23 |
| **11** | 85.40 | 0.02 | 0.09 | 0.00 | 0.00 | 0.00 | 0.02 | 0.00 | 0.04 | 0.00 | 0.05 | 85.61 |
| **12** | 61.42 | 0.42 | 25.19 | 0.00 | 0.00 | 0.08 | 0.06 | 0.00 | 0.05 | 0.00 | 0.00 | 87.22 |
| **13** | 85.91 | 0.04 | 0.44 | 0.00 | 8.98 | 0.01 | 0.03 | 0.00 | 0.20 | 0.04 | 0.07 | 95.70 |
| **14** | 38.94 | 0.84 | 37.01 | 0.15 | 0.00 | 0.22 | 0.05 | 0.00 | 0.05 | 0.00 | 0.26 | 77.51 |
| **15** | 76.66 | 0.11 | 1.28 | 0.00 | 0.00 | 0.05 | 0.07 | 0.00 | 0.15 | 0.01 | 0.00 | 78.33 |
| **16** | 37.71 | 0.76 | 31.53 | 0.03 | 0.00 | 0.19 | 0.04 | 0.00 | 0.03 | 0.00 | 0.00 | 70.28 |
| **17** | 62.91 | 0.23 | 9.89 | 0.04 | 1.08 | 0.12 | 0.21 | 0.00 | 0.51 | 0.09 | 0.11 | 75.18 |
| **18** | 53.03 | 0.33 | 12.33 | 0.00 | 0.00 | 0.16 | 0.19 | 0.00 | 0.14 | 0.02 | 0.00 | 66.19 |

## SUMMARY

It is a binary alloy of Cu-Sn with an equi-axed structure. The original tin content is about 10-15% based on EPMA and SEM/EDS data. It is deeply corroded with isolated α grains being preserved. Both intergranular and intragranular corrosion is present.

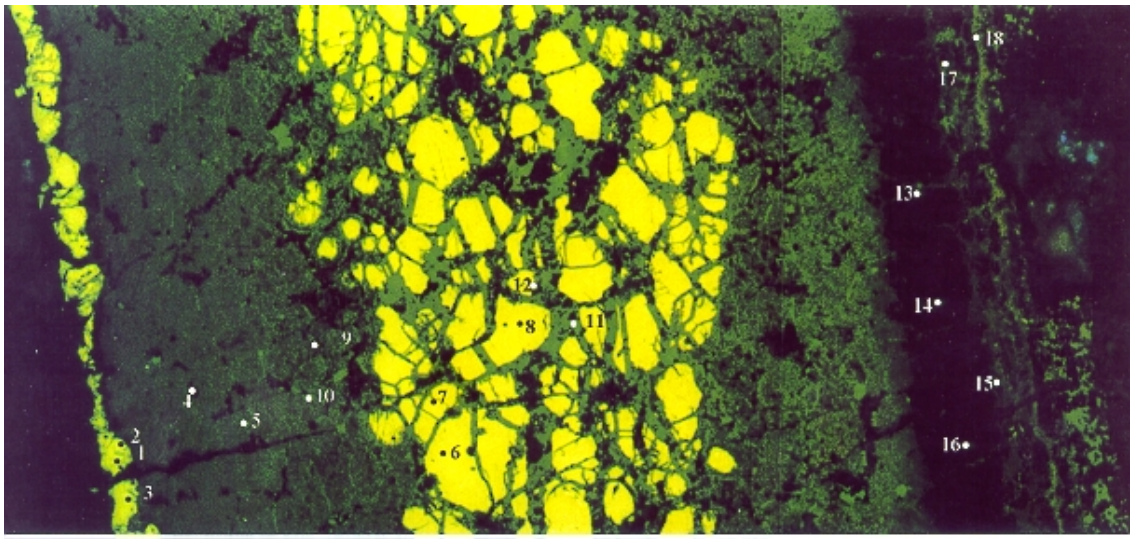



Fig. 3 Photomicrograph of the corroded metal, showing an equi-axed structure and EPMA points. BF. Width of the image = 1.2 mm.

## GENERAL

**Object Number:** M6190:3
**Excavation Date:** 1984
**Origin:** Tianma-Qucun site

**Object:** vessel/*gui* (Fig. 1)
**Date:** Early Western Zhou
**Fragment Weight:** 1.0 g
**Fragment size:** 12x7x1.3 mm

**General description:**

This fragment was from a sidewall. It has all sides broken. Corrosion index is 5. It looks different from normal bronzes in colour. There is a silvery layer, possibly solder on a surface. Most of the original surface is covered with a powdery silvery layer; the other areas are covered with yellow materials (Figs. 2 & 3). No decoration is apparent.

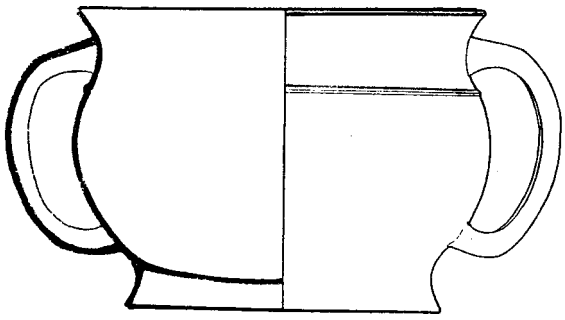


Fig. 1 The object

## TECHNICAL STUDIES OF METAL

**Metallographic structure:**

A section cut through the full width of the fragment across the silvery layer was taken for metallographic observation. The original surfaces can be seen. The estimated thickness is 1.3 mm as measured in the metallographic section. Its microstructure is not evident (Fig. 4).

**Composition:**

**AAS:** too corroded for analysis

**Microanalysis:**

See corrosion section

**Microhardness:** too corroded for measuring

Fig. 2 General view of silvery layer on an original surface of the fragment.
Width of the image = 14 mm.

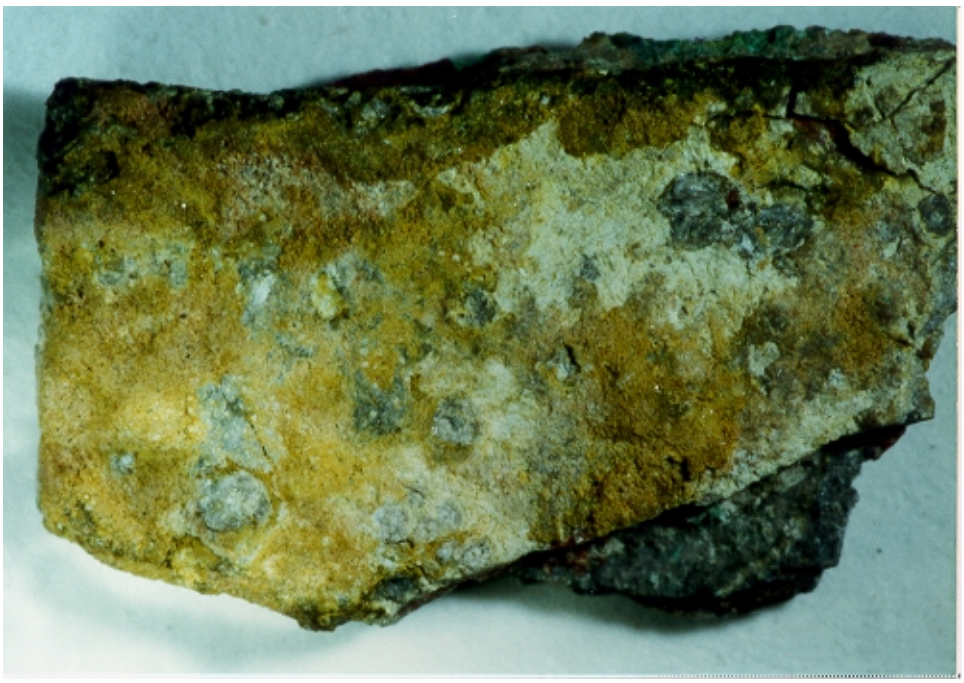


Fig. 3 General view of the other original surface of the fragment.
Width of the image = 14 mm.

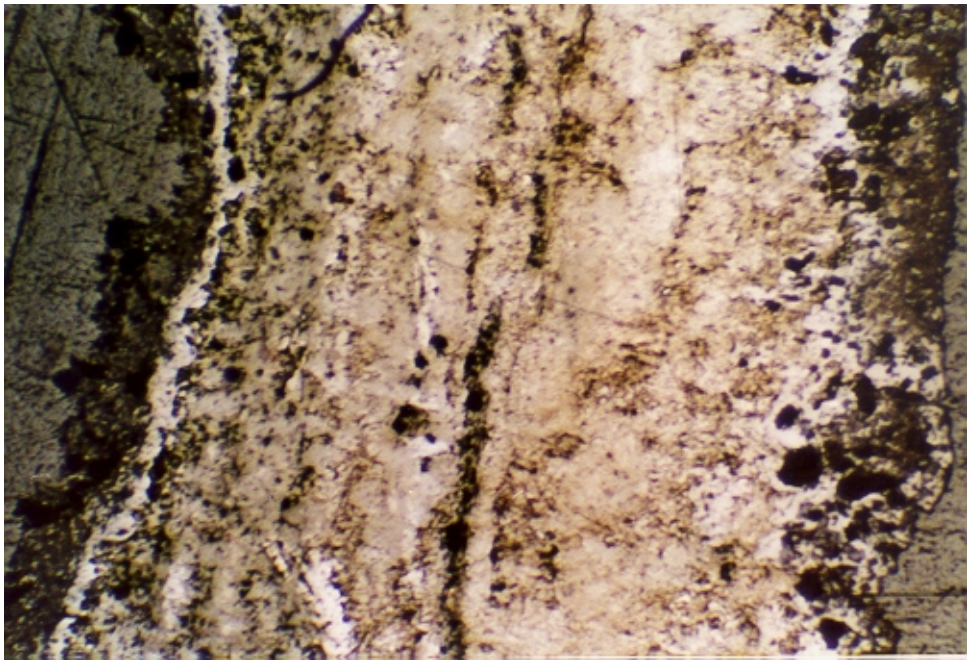


Fig. 4 Photomicrograph of the section. Microstructure is not evident.
BF. Width of the image = 2 mm.

## CORROSION

### XRD results:

Silvery material: mainly cerussite, with presence of quartz and $Pb_3(CO_3)_2(OH)_2$.

Material on the other surface: mainly cerussite, with presence of $Pb_3(CO_3)_2(OH)_2$.

### Metallographic observation:

It is deeply corroded, no metallic phase is seen at all. It is very porous, grey colour in bright field (Fig. 4), but appears yellow to red colour in cross polarised light.

### Microanalysis:

XRF analysis shows this silvery layer contains mainly Pb and a bit of Cu.

EPMA was carried out. Backscattered electron image shows a surface layer at the top (Fig. 5), but it does not show a difference in composition from other areas (see below data). This sample was easily damaged by electron beams (Fig. 6, the square at

bottom). 22 points from surface inward and several points (A – J) in center of the piece were analysed; the results are as follows:

| Point | Cu | Ni | Fe | Sn | Pb | As | Zn | Co | S | Cl | Sb | Bi | Ag | Hg | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 0.00 | 0.00 | 0.03 | 0.00 | 75.08 | 0.00 | 0.00 | 0.00 | 0.00 | 0.04 | 0.00 | 0.00 | 0.00 | 0.00 | 75.16 |
| **2** | 0.00 | 0.01 | 0.05 | 0.01 | 83.78 | 0.00 | 0.00 | 0.00 | 0.00 | 0.04 | 0.00 | 0.00 | 0.00 | 0.00 | 83.89 |
| **3** | 0.03 | 0.01 | 0.07 | 0.02 | 84.24 | 0.00 | 0.00 | 0.00 | 0.17 | 2.19 | 0.00 | 0.00 | 0.00 | 0.00 | 86.73 |
| **4** | 3.15 | 0.01 | 0.06 | 0.01 | 79.52 | 0.00 | 0.00 | 0.00 | 1.49 | 0.12 | 0.00 | 0.00 | 0.00 | 0.00 | 84.36 |
| **5** | 0.50 | 0.00 | 0.05 | 0.00 | 78.39 | 0.00 | 0.00 | 0.00 | 0.00 | 0.37 | 0.00 | 0.00 | 1.31 | 0.00 | 80.62 |
| **6** | 0.00 | 0.01 | 0.05 | 0.00 | 82.23 | 0.00 | 0.00 | 0.00 | 0.00 | 0.35 | 0.00 | 0.00 | 0.85 | 0.00 | 83.49 |
| **7** | 0.02 | 0.00 | 0.08 | 0.01 | 84.67 | 0.00 | 0.00 | 0.00 | 0.00 | 0.11 | 0.00 | 0.00 | 0.00 | 0.00 | 84.89 |
| **8** | 0.00 | 0.01 | 0.07 | 0.00 | 87.66 | 0.00 | 0.00 | 0.01 | 0.00 | 0.44 | 0.00 | 0.00 | 0.00 | 0.00 | 88.20 |
| **9** | 0.10 | 0.01 | 0.06 | 0.01 | 83.93 | 0.00 | 0.00 | 0.00 | 0.00 | 0.18 | 0.00 | 0.00 | 0.00 | 0.00 | 84.30 |
| **10** | 1.20 | 0.00 | 0.06 | 0.01 | 81.81 | 0.00 | 0.00 | 0.01 | 0.00 | 0.07 | 0.00 | 0.00 | 0.00 | 0.00 | 83.16 |
| **11** | 1.15 | 0.02 | 0.06 | 0.00 | 84.04 | 0.00 | 0.00 | 0.00 | 0.00 | 0.13 | 0.00 | 0.00 | 0.00 | 0.00 | 85.38 |
| **12** | 0.02 | 0.00 | 0.06 | 0.00 | 88.77 | 0.03 | 0.00 | 0.01 | 0.00 | 0.12 | 0.00 | 0.00 | 0.11 | 0.00 | 89.13 |
| **13** | 0.02 | 0.00 | 0.06 | 0.01 | 85.42 | 0.00 | 0.00 | 0.00 | 0.00 | 0.07 | 0.00 | 0.00 | 0.00 | 0.00 | 85.58 |
| **14** | 0.00 | 0.00 | 0.06 | 0.00 | 82.12 | 0.47 | 0.00 | 0.00 | 0.00 | 0.05 | 0.00 | 0.00 | 0.00 | 0.00 | 82.70 |
| **15** | 0.03 | 0.00 | 0.05 | 0.00 | 82.66 | 0.00 | 0.00 | 0.00 | 0.00 | 0.20 | 0.00 | 0.00 | 0.12 | 0.00 | 83.05 |
| **16** | 0.03 | 0.01 | 0.06 | 0.02 | 85.67 | 0.00 | 0.00 | 0.00 | 0.00 | 1.06 | 0.00 | 0.64 | 0.00 | 0.00 | 87.48 |
| **18** | 0.13 | 0.00 | 0.07 | 0.00 | 83.99 | 0.00 | 0.00 | 0.00 | 0.00 | 0.32 | 0.00 | 0.80 | 0.00 | 0.00 | 85.32 |
| **19** | 0.11 | 0.00 | 0.05 | 0.00 | 83.82 | 0.00 | 0.00 | 0.00 | 0.00 | 0.04 | 0.00 | 0.00 | 0.00 | 0.00 | 84.03 |
| **20** | 0.01 | 0.00 | 0.07 | 0.03 | 84.18 | 0.00 | 0.00 | 0.00 | 0.00 | 0.43 | 0.00 | 2.10 | 0.00 | 0.00 | 86.81 |
| **21** | 0.00 | 0.00 | 0.08 | 0.03 | 88.46 | 2.90 | 0.00 | 0.00 | 0.00 | 0.96 | 0.00 | 0.00 | 0.00 | 0.00 | 92.43 |
| **22** | 0.39 | 0.00 | 0.05 | 0.00 | 87.44 | 0.00 | 0.00 | 0.00 | 0.00 | 0.13 | 0.00 | 0.37 | 0.00 | 0.00 | 88.38 |
| | | | | | | | | | | | | | | | |
| **A** | 0.00 | 0.00 | 0.08 | 0.00 | 91.39 | 0.00 | 0.00 | 0.00 | 0.00 | 0.06 | 0.00 | 0.00 | 0.00 | 0.00 | 91.53 |
| **B** | 0.13 | 0.00 | 0.04 | 0.01 | 82.28 | 0.00 | 0.00 | 0.00 | 0.00 | 0.10 | 0.00 | 0.00 | 0.00 | 0.00 | 82.56 |
| **C** | 0.00 | 0.00 | 0.06 | 0.00 | 83.93 | 0.00 | 0.00 | 0.00 | 0.00 | 0.12 | 0.00 | 0.05 | 0.00 | 0.00 | 84.16 |
| **D** | 0.00 | 0.00 | 0.08 | 0.01 | 89.07 | 0.00 | 0.00 | 0.00 | 0.00 | 0.14 | 0.00 | 0.07 | 0.00 | 0.00 | 89.36 |
| **E** | 0.00 | 0.02 | 0.05 | 0.00 | 89.79 | 0.00 | 0.00 | 0.01 | 0.00 | 0.14 | 0.00 | 0.00 | 0.00 | 0.00 | 90.01 |
| **F** | 0.05 | 0.01 | 0.08 | 0.00 | 85.47 | 0.00 | 0.00 | 0.00 | 0.00 | 0.72 | 0.00 | 0.00 | 2.23 | 0.00 | 88.56 |
| **G** | 0.01 | 0.00 | 0.07 | 0.00 | 92.49 | 0.00 | 0.00 | 0.00 | 0.00 | 0.05 | 0.00 | 0.00 | 0.00 | 0.00 | 92.62 |
| **H** | 0.04 | 0.01 | 0.06 | 0.03 | 86.17 | 0.00 | 0.00 | 0.01 | 0.00 | 0.09 | 0.00 | 0.09 | 0.00 | 0.00 | 86.49 |
| **I** | 0.01 | 0.00 | 0.05 | 0.00 | 86.45 | 0.00 | 0.00 | 0.00 | 0.00 | 0.06 | 0.00 | 0.00 | 0.00 | 0.00 | 86.58 |
| **J** | 0.05 | 0.00 | 0.06 | 0.01 | 91.03 | 0.00 | 0.00 | 0.00 | 0.00 | 0.06 | 0.00 | 0.00 | 0.00 | 0.00 | 91.21 |

Above results indicate that this is a lead object. EPMA data on the surface are identical with XRD results (Cerussite contains 77.5% Pb, and $Pb_3(CO_3)_2(OH)_2$ contains 80.2% Pb). The higher content of Pb, e.g. 92.5% (point G) is probably due to partial corrosion of the analysed points)

## SUMMARY

It is a lead object with an unidentified structure due to corrosion. The main corrosion product is cerussite with lead hydrocarbonate.

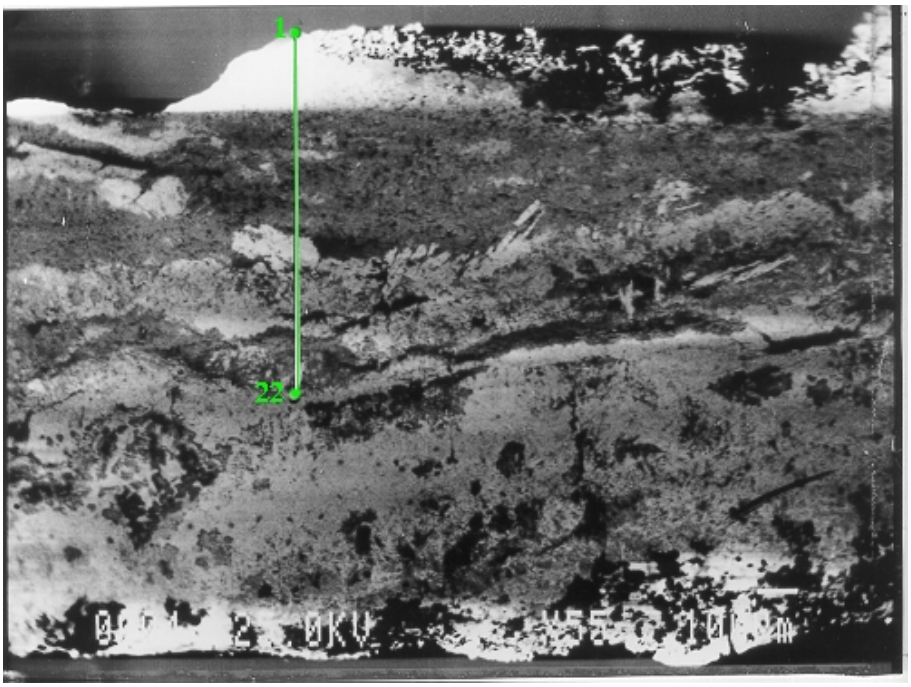



Fig. 5 BEI of the metallographic section, showing EPMA points 1 – 22.

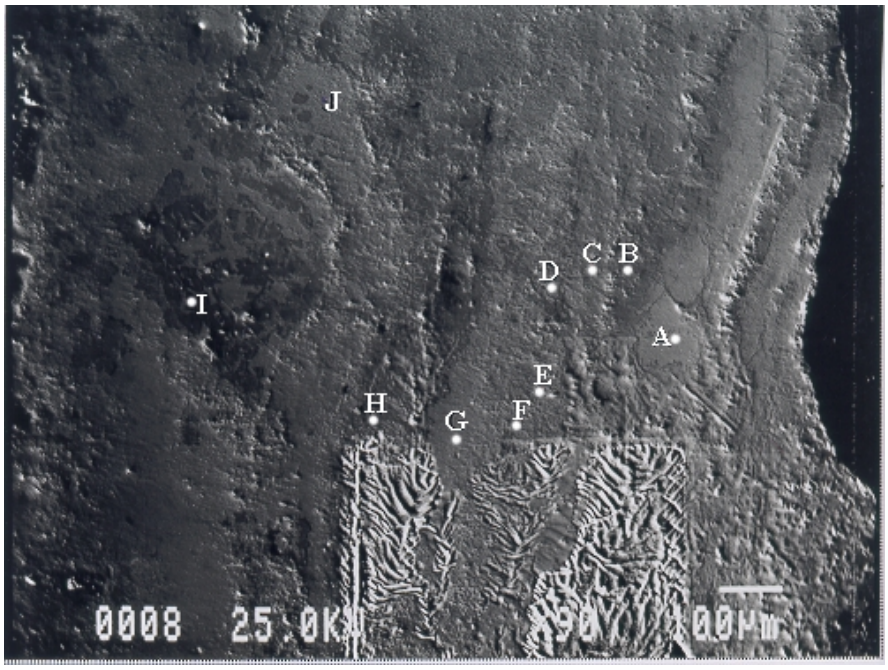



Fig. 6 SEI of corroded metal, showing EPMA points and the damaged area by electron beams.

## GENERAL

**Object Number:** M6372:unknown
**Excavation Date:** 1986
**Origin:** Tianma-Qucun site

**Object:** unknown
**Date:** Early Western Zhou
**Fragment Weight:** 0.8 g
**Fragment size:** 10x8x? mm

**General description:**

There are several fragments, probably from a tin object. All sides of each fragment are broken. Corrosion index is 5. These fragments are very fragile with fractures (Fig. 1).

## TECHNICAL STUDIES OF METAL

**Metallographic structure:**

The fragment shown in Fig. 1 was taken for metallographic observation. The original surfaces are hardly seen. Its original dimensions are difficult to estimate due to expansion (Fig. 2). A few areas of metallic phases are seen (Fig. 3). The presence of remnant metallic phases along boundaries (Fig. 4) and its colour indicate that it was grey cubic form of tin (XRD and EPMA confirmed that it is a tin object).

Fig. 1 General view of the fragment.
Width of the image = 14 mm.

Fig. 2 The metallographic section.
Width of the image = 6 mm.

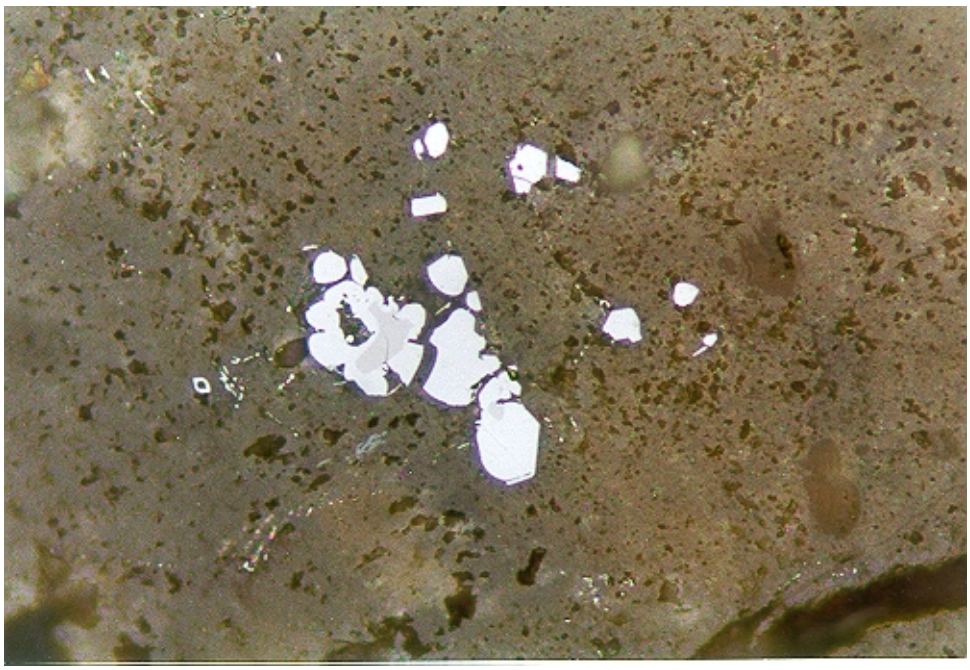


Fig. 3 Remnant metallic phase, showing different brightness.
BF. Width of the image = 0.2 mm.

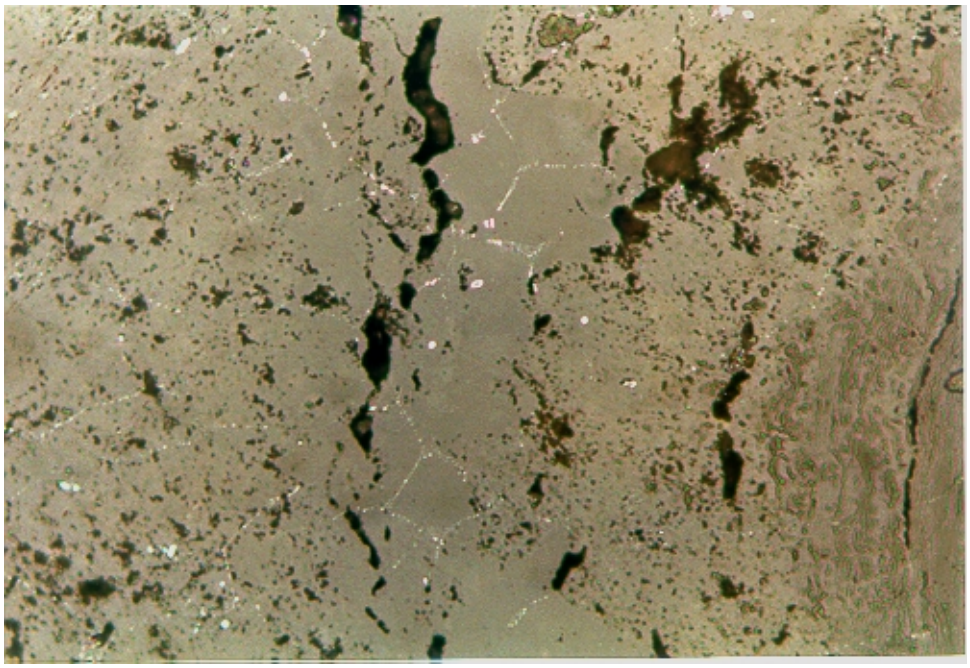


Fig. 4 Microstructure of the corroded metal, showing grain boundaries.
BF. Width of the image = 0.5 mm.

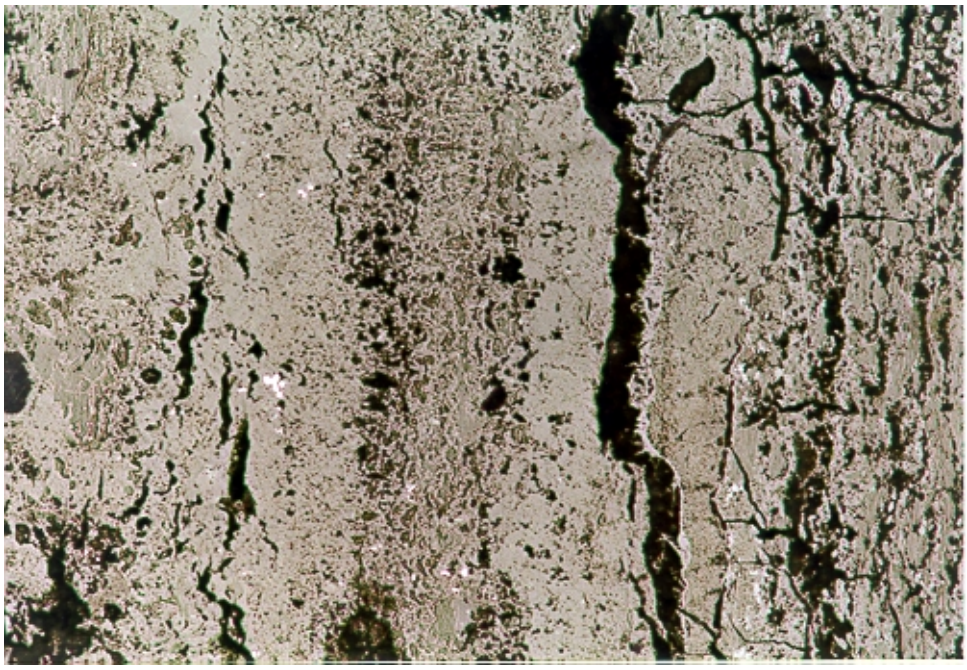


Fig. 5 Photomicrograph of cracks in the corroded metal.
BF. Width of the image = 2 mm.

**Composition:**

**AAS:** too corroded for analysis.

**Microanalysis:**

See corrosion section.

**Microhardness:** too corroded for measuring.

**CORROSION**

**XRD results:** cassiterite.

**Metallographic observation:**

It is totally corroded and very porous. Fractures are present. It is grey in bright field, and appears black in cross polars. A banded structure is also seen (on right side of Fig. 5).

**Microanalysis:**

EPMA was carried out on the corroded metal (Figs. 6 & 7). The results show that the metallic phase is comprised of Sn and Fe. Moreover, the darker area (containing about 31% Fe, approximately the concentration of Fe in FeSn) of the metallic phase is of more Fe than the lighter area (containing about 18% Fe, approximately the concentration of Fe in $FeSn_2$). This assumes that the original Fe content could be in the range of 18-32% Fe. Alternatively, the original content of Fe could be lower than 18% if this resulted from a fast cooling. According to Fe-Sn diagram (Fig. 8), FeSn forms when temperature drops to about 760°C. When temperature drops further to about 500°C, peritectic reaction takes place to transfer FeSn to $FeSn_2$. This reaction does not complete when the system is fast cooled, so FeSn is partially preserved.

The major corrosion product contains mainly Sn, this is identical with the XRD result, although the concentration of Sn varies a little due to its different densities. The banded structure does not show much difference in composition from other parts. The fact that Fe is only present in the remnant metallic phases suggests that it is the result of segregation during manufacture process.

| Point | Description |
|---|---|
| **1, 4, 5** | Lighter area of the metallic phase |
| **2, 3** | Darker area of the metallic phase |
| **6, 7, 8** | Cassiterite |

| Point | Cu | Fe | Sn | Pb | S | Cl | Ag | Bi | As | Total |
|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 0.02 | 19.45 | 73.53 | 0.00 | 0.03 | 0.00 | 0.00 | 0.04 | 0.00 | 93.07 |
| **2** | 0.00 | 30.86 | 63.99 | 0.00 | 0.00 | 0.00 | 0.00 | 0.11 | 0.00 | 94.96 |
| **3** | 0.03 | 31.15 | 65.42 | 0.13 | 0.01 | 0.00 | 0.00 | 0.12 | 0.00 | 96.85 |
| **4** | 0.03 | 18.90 | 79.25 | 0.02 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 98.20 |
| **5** | 0.04 | 18.69 | 76.49 | 0.00 | 0.12 | 0.01 | 0.00 | 0.10 | 0.00 | 95.45 |
| **6** | 0.06 | 0.03 | 70.82 | 0.09 | 0.10 | 0.08 | 0.00 | 0.03 | 0.00 | 71.19 |
| **7** | 0.11 | 0.01 | 71.56 | 0.07 | 0.05 | 0.05 | 0.00 | 0.15 | 0.00 | 71.99 |
| **8** | 0.02 | 0.00 | 64.37 | 0.26 | 0.03 | 0.04 | 0.00 | 0.08 | 0.00 | 64.79 |

Qualitative analysis using microprobe was carried out on an area of 25 μm (2000 steps, 2sec/step) to check Ta, Nb, Ni, Zn, and Co, the results show that these elements are absent.

## SUMMARY

It was a tin object. It is totally corroded and converted to cassiterite. Only a little of isolated metallic phases have been preserved. The metallic phase contains Sn and Fe.

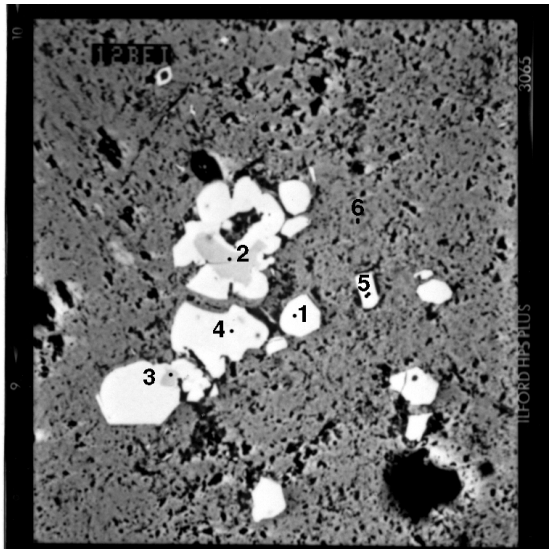



Fig. 6 BEI of remnant metallic phase, Showing EPMA points.

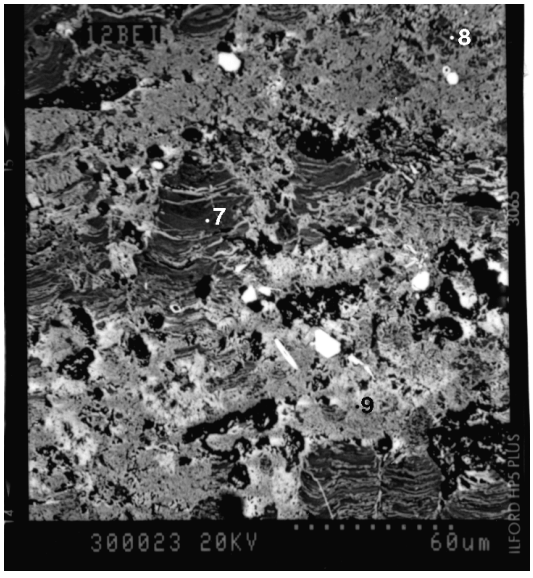



Fig. 7 BEI of corroded metal, showing EPMA points.

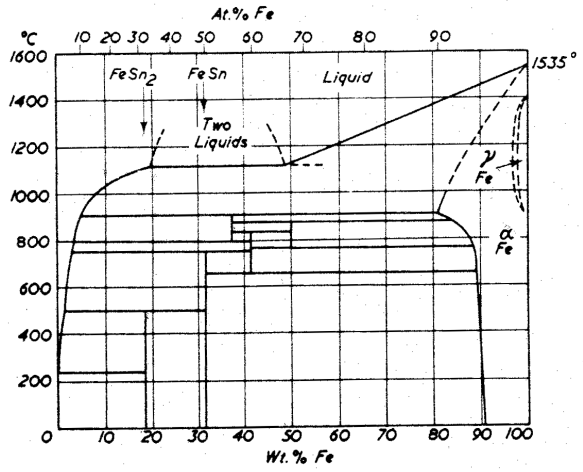



Fig. 8 Diagram of Fe-Sn system (after Brandes, 1983, 11-258)

## GENERAL

**Object Number:** M6384:20
**Excavation Date:** 1986
**Origin:** Tianma-Qucun site

**Object:** horse fitting/*luan* bell
**Date:** Early or middleWestern Zhou
**Fragment Weight:** 0.8 g
**Fragment size:** 6x5x2.3 mm

**General description:**

This fragment has two sides broken, Corrosion index is 3. There is a corrosion overburden, including metallic lustrous material on the original surfaces (Fig. 1). The lustrous material is seen in spots all over the cross section of the fragment (Fig. 2). The original surfaces are covered with blue, green and yellow corrosion products. No decoration is apparent.

## TECHNICAL STUDIES OF METAL

**Metallographic structure:**

The whole piece was mounted with cross section facing down and then sectioned through the full width across the metallic lustrous material. The cut surface was taken for metallographic observation. The estimated thickness is 2.3 mm as measured in the metallographic section. It has a dendritic structure with redeposited Cu (Fig. 3).

**Composition:**

**AAS:**

| Cu | Sn | Pb | Fe | As | Co | Zn | Ni | Ag | Au | Sb | Bi | total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ( | wt% | | ) | ( | | | ppm | | | | ) | (wt%) |
| 80.66 | 16.83 | 0.18 | 0.78 | nd | nd | 519 | 118 | 708 | nd | nd | nd | 98.57 |

**Microanalysis:**

See corrosion section.

**Microhardness:** 182Hv

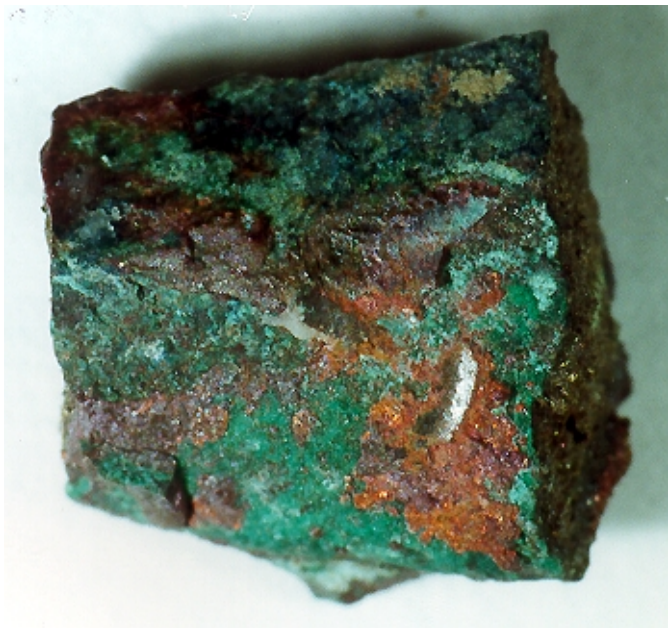


Fig. 1 General view of original surface of the fragment, showing metallic lustrous materials.
Fragment size = 6x5 mm.

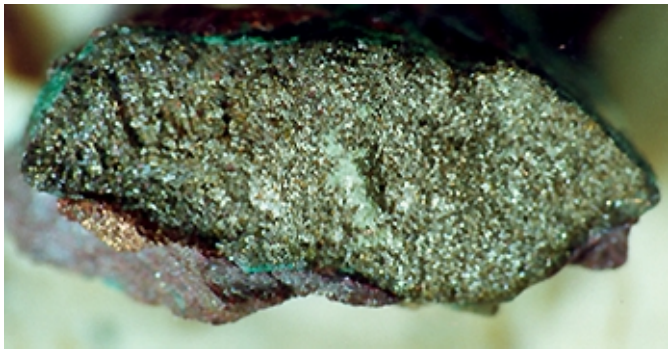


Fig. 2 General view of cross section of the fragment, showing metallic lustrous spots. Width of the image = 7 mm.

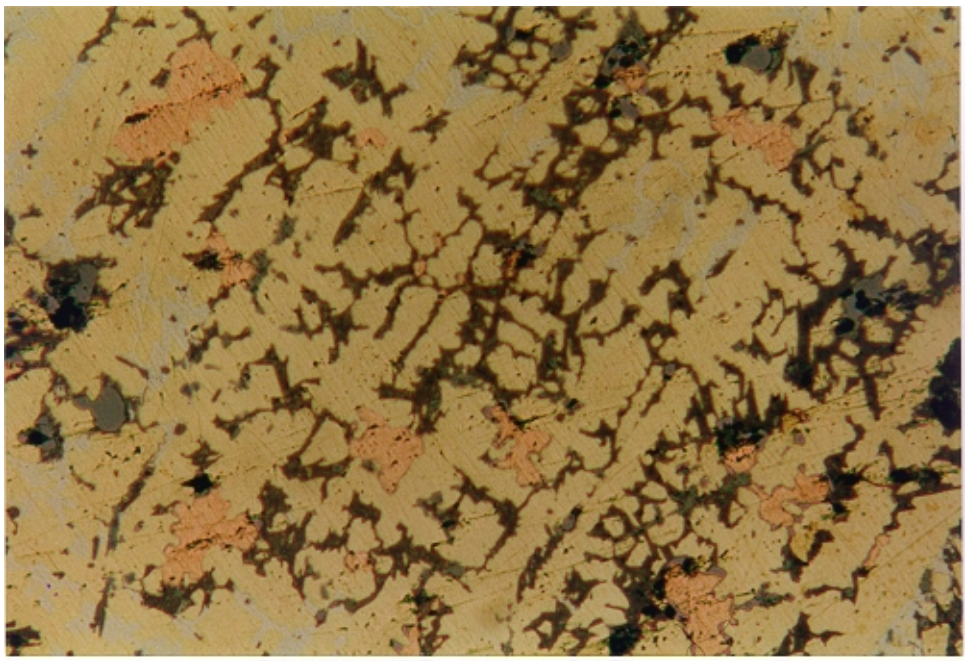


Fig. 3 Dendritic microstructure of corroded metal. BF. Width of the image = 0.5 mm.

## CORROSION

**XRD results:** not carried out.

**Metallographic observation:**

It is deeply corroded, with corrosion penetrating throughout the cross section in some areas (Fig. 4). On the original surfaces, a band of redeposited Cu (confirmed by EPMA) is present on each side, immediately next to the metal (Fig. 4). Therefore, the matallic lustrous material on the surface must be redeposited Cu. In the corroded metal, eutectoids are gone. Corrosion overburden is thick on one surface, it is a interlaced structure, mainly comprised of cuprite, cassiterite and copper carbonate based on their characteristic colours in the metallographic section (Fig. 5).

**Microanalysis:**

EPMA was carried out on metal, redeposited Cu bands and corrosion overburden, the results are as follows (the analyzed points are not marked because of the wide range of areas analyzed). Bronze disease was not found.

| Point | Description |
|---|---|
| **1, 4, 5** | Redepodited Cu |
| **2** | Corroded α phase |
| **3** | δ phase |
| **6, 7, 8** | Corrosion overburden |

| Point | Cu | Fe | Au | Ni | Sn | Pb | Zn | Ag | Hg | As | Sb | Bi | Co | S | Cl | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 90.43 | 0.03 | 0.03 | 0.00 | 0.05 | 0.00 | 0.00 | 0.13 | 0.00 | 0.00 | 0.00 | 0.11 | 0.00 | 0.00 | 0.00 | 90.78 |
| **2** | 64.69 | 0.88 | 0.00 | 0.00 | 12.57 | 0.06 | 0.01 | 0.06 | 0.00 | 0.00 | 0.00 | 0.04 | 0.01 | 0.00 | 0.00 | 78.33 |
| **3** | 54.26 | 0.26 | 0.08 | 0.02 | 34.68 | 0.66 | 0.00 | 0.09 | 0.00 | 0.06 | 0.00 | 0.08 | 0.00 | 0.11 | 0.04 | 90.32 |
| **4** | 91.52 | 0.01 | 0.03 | 0.00 | 0.00 | 0.00 | 0.00 | 0.12 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 91.68 |
| **5** | 91.63 | 0.01 | 0.01 | 0.00 | 0.04 | 0.12 | 0.00 | 0.09 | 0.00 | 0.00 | 0.01 | 0.06 | 0.00 | 0.00 | 0.00 | 91.96 |
| **6** | 43.29 | 1.86 | 0.02 | 0.00 | 26.12 | 0.21 | 0.00 | 0.20 | 0.00 | 0.03 | 0.00 | 0.08 | 0.00 | 1.43 | 0.23 | 73.47 |
| **7** | 26.04 | 1.59 | 0.02 | 0.00 | 34.49 | 0.38 | 0.00 | 0.02 | 0.00 | 0.00 | 0.00 | 0.06 | 0.00 | 0.04 | 0.00 | 62.63 |
| **8** | 36.48 | 2.20 | 0.00 | 0.01 | 32.47 | 0.22 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.05 | 0.04 | 71.47 |

## SUMMARY

It is a binary alloy of Cu-Sn with a dendritic structure. The original composition determined by AAS is 80.7% Cu and 16.8% Sn. Redeposited Cu is present both inside the metal and on the surface. A band of redeposited Cu is seen on each of the original surfaces.

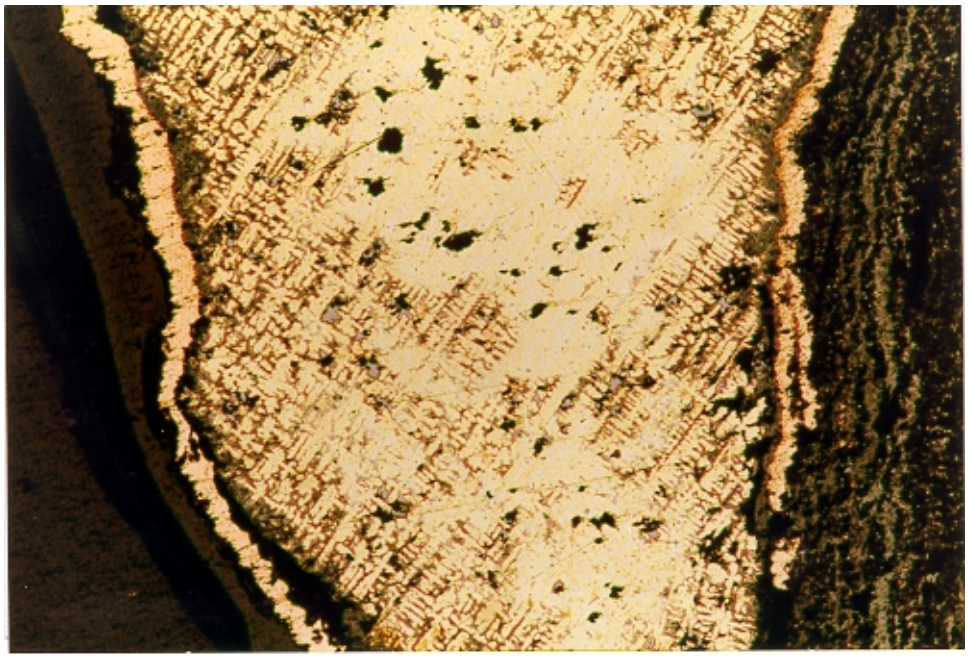


Fig. 4 Photomicrograph of redeposited Cu bands on the surface.
BF. Width of the image = 2 mm.

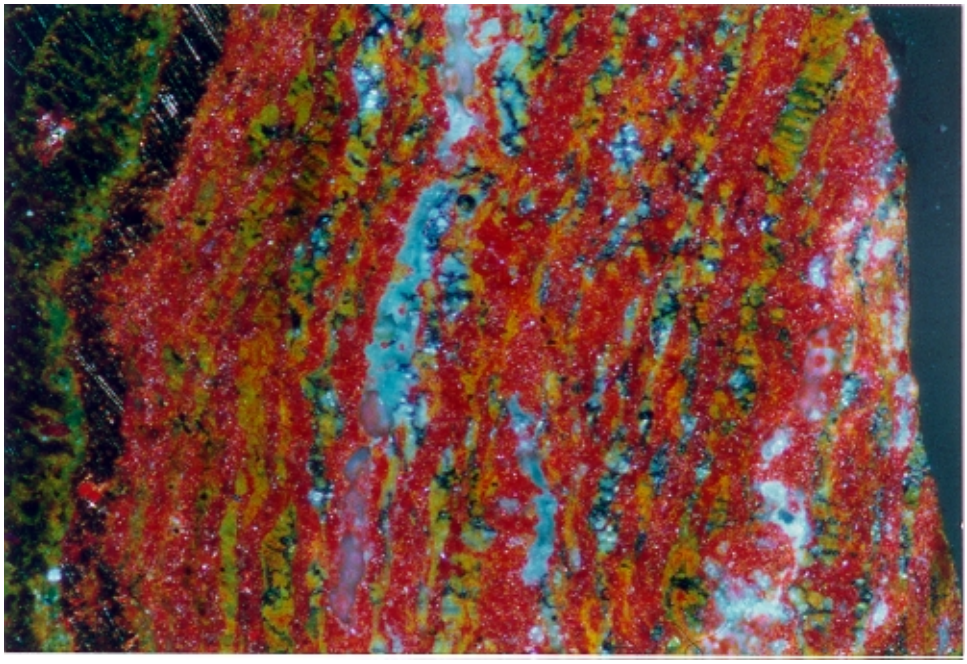


Fig. 5 Photomicrograph of interlaced corrosion products in overburden.
C/P. Width of the image = 0.9 mm.

## GENERAL

**Object Number:** M6384:unknown
**Excavation Date:** 1986
**Origin:** Tianma-Qucun site

**Object:** unknown
**Date:** Early or middleWestern Zhou
**Fragment Weight:** 4.0 g
**Fragment size:** 23x22x1.5 mm

**General description:**

Three fragments were provided for analysis. The appearance of the biggest one is different from the others (Fig. 1). It was taken for study. It has all sides broken. Corrosion index is 4. There is a corrosion overburden on the surface, including powdery green and red corrosion products and soil. Fibrous materials are also observed on the surface (Fig. 2). X-radiography shows decoration patterns on the outer surface. The patterns are visible after mechanical cleaning (Fig. 3). The angle between 2 edges is about 120°. It was probably from a vessel such as *ding* or *li* based on the type of patterns.

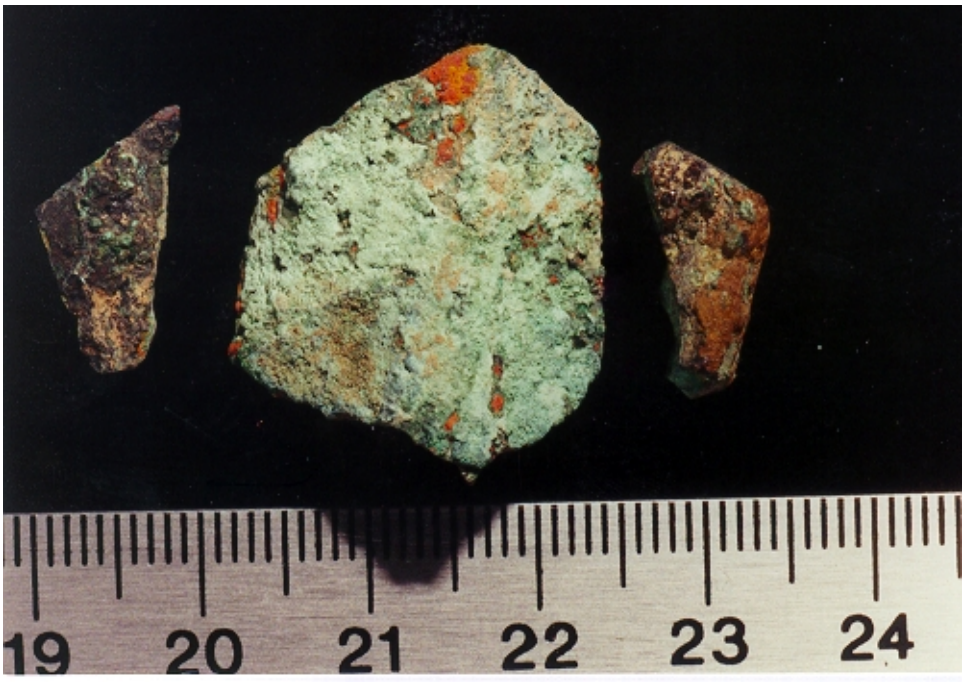



Fig. 1 General view of the fragments.

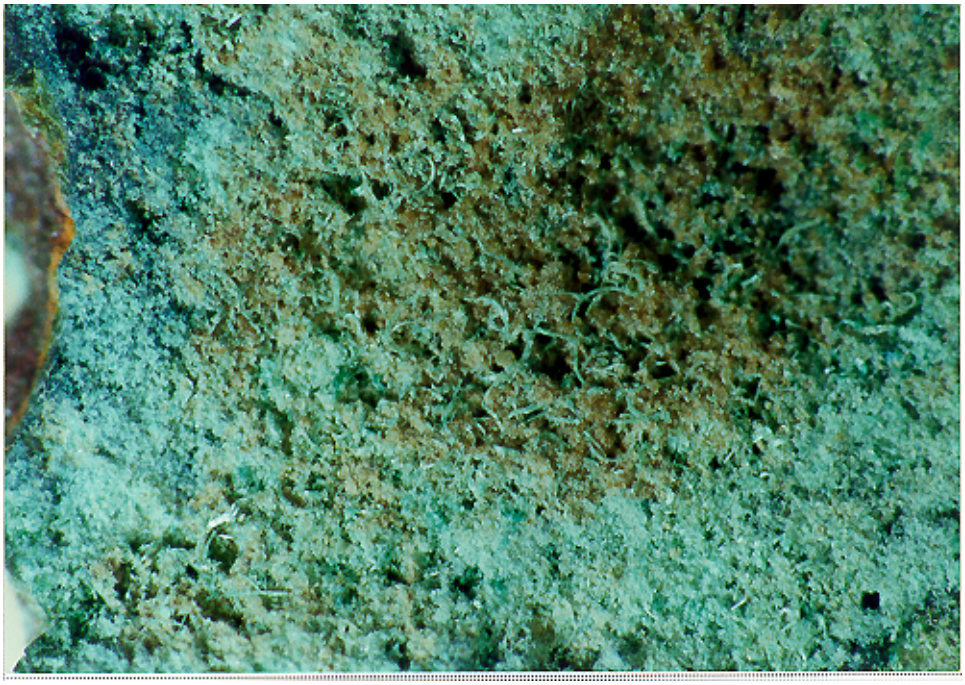


Fig. 2 Fibrous materials seen on surfaces of the fragment.
Width of the image = 5.5 mm.

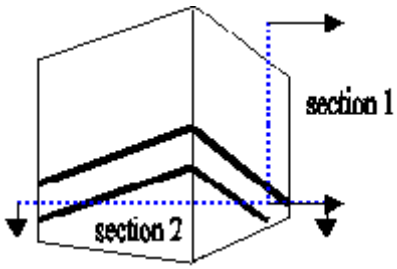



Fig. 3 Decoration patterns on the surface (size = 23x22 mm).
Two sections were taken for metallographic observation.

## TECHNICAL STUDIES OF METAL

### Metallographic structure:

Two sections shown in Fig. 3 were taken for metallographic observation. Metallographic observation shows no difference in microstructure between these two sections. They both have an equi-axed structure with no evidence of working. Therefore, section 1 was taken for further studies. The original surfaces are disrupted (Fig. 4). The estimated thickness is 1.5 mm as measured in the metallographic section. The estimated grain size is 0.041 mm.

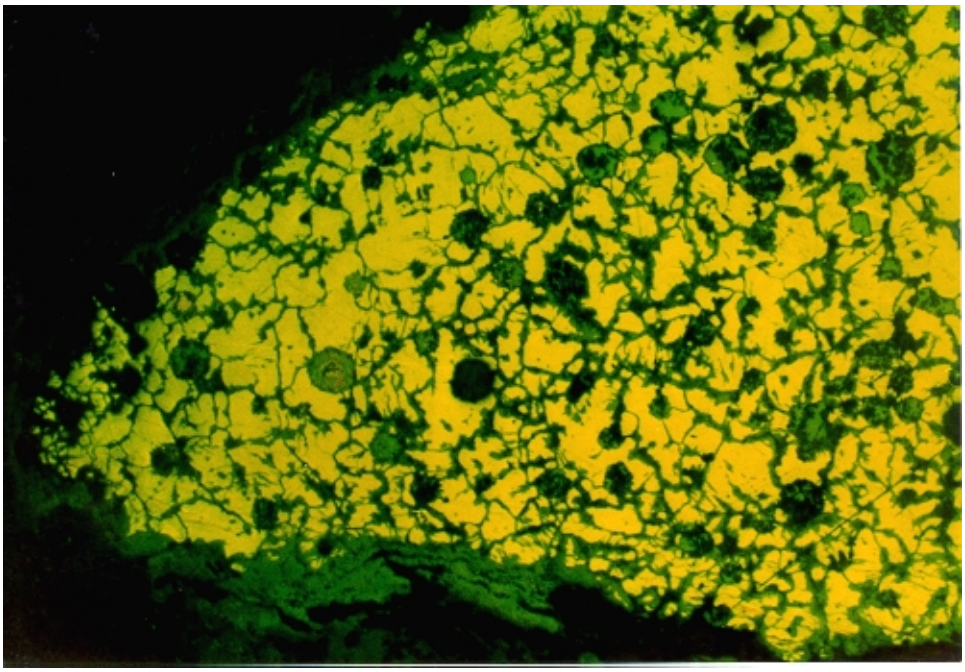


Fig. 4 Equi-axed microstructure of the corroded metal, showing disrupted surfaces. BF. Width of the image = 2 mm.

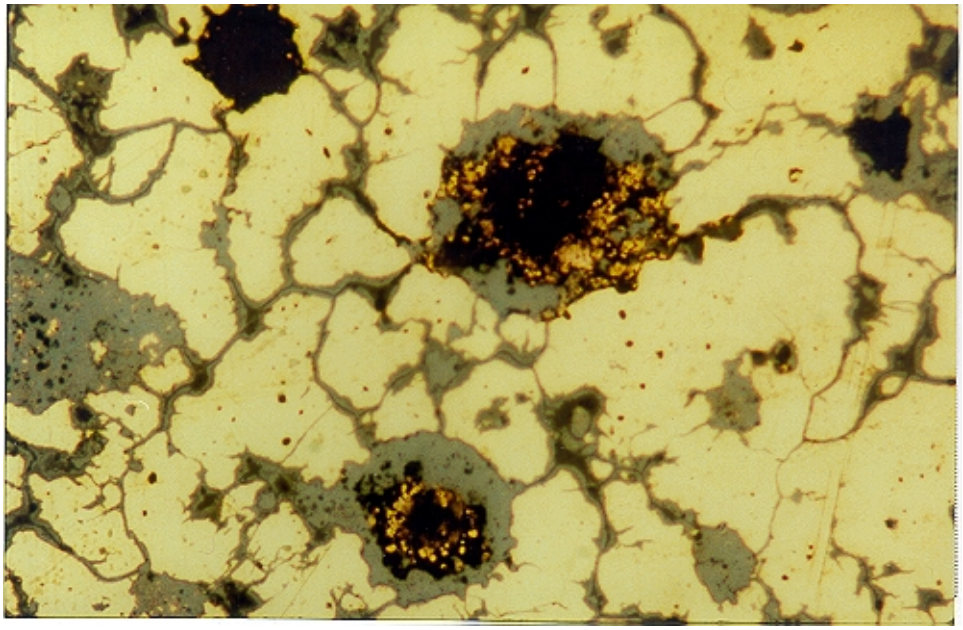


Fig. 5 Photomicrograph of the corroded metal, showing redeposited Cu within cuprit and intergranular corrosion. BF. Width of the image = 0.5 mm.

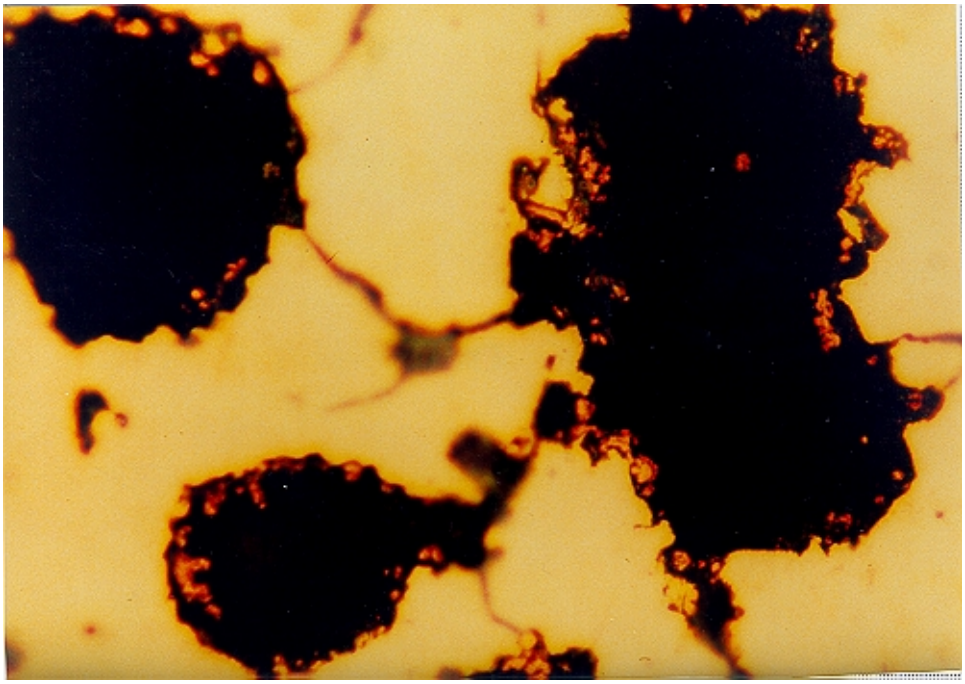


Fig. 6 Photomicrograph redeposited Cu with nantokite.

BF. Width of the image = 0. 2 mm.

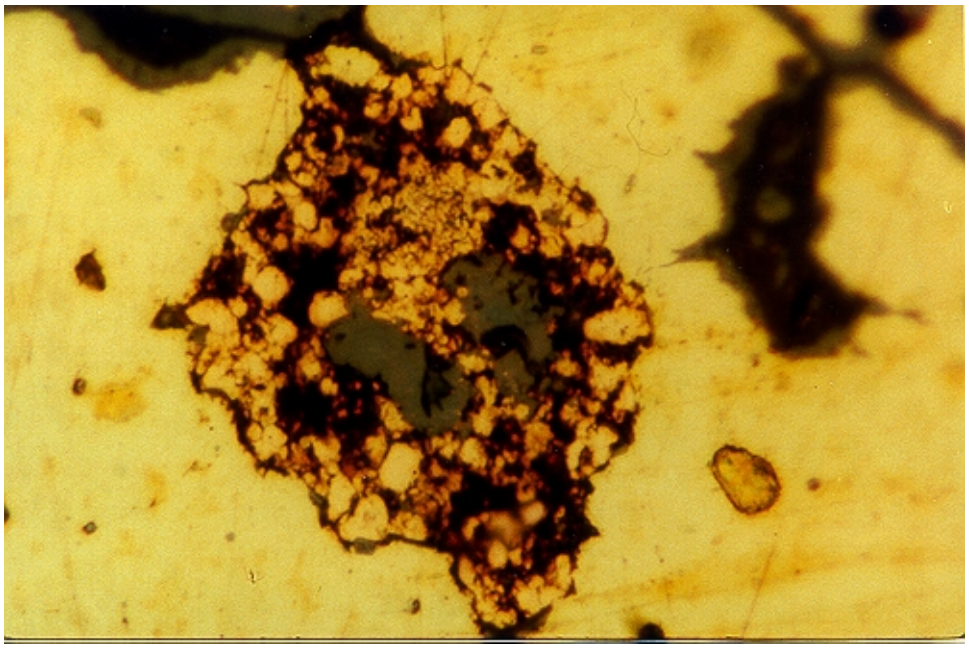


Fig. 7 Photomicrograph of redeposited Cu with cuprite.

BF. Width of the image = 0.1 mm.

## Composition:

**AAS:**

| Cu | Sn | Pb | Fe | As | Co | Zn | Ni | Ag | Au | Sb | Bi | total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ( | wt% | | ) | ( | | | ppm | | | | ) | (wt%) |
| 75.00 | 11.61 | 0.19 | 0.16 | nd | nd | 818 | nd | 2273 | nd | nd | nd | 87.28 |

The low total is due to corrosion of this sample. Intergranular corrosion is evident in Fig. 4 & 5.

**Microanalysis:**

See corrosion section.

**Microhardness:** 103Hv

## CORROSION

### XRD results:

Surface sample: malachite, cuprite, brochantite.

### Metallographic observation:

It is deeply corroded, with corrosion penetrating through the whole section (Fig. 4). Corrosion pits are present inside the metal. Redeposited Cu is seen in some of the corrosion pits (Figs. 5 & 6). Redeposited Cu replaced most cuprite in some areas (Fig. 7). Some corrosion pits look like holes (Fig. 6).

### Microanalysis:

EPMA was carried out on both corroded metal and corrosion on surfaces (Figs. 8 & 9), the results are as follows:

| Point | Description |
|---|---|
| **1, 2, 11, 14** | Corroded grain boundary |
| **3, 6, 12** | α phase |
| **4, 5, 7, 8, 9, 10** | Nantokite |
| **13** | Cuprite |
| **15 - 19** | Corrosion on a surface |
| **20 - 24** | Corrosion on the other surface |

| Point | Cu | Fe | Sn | Pb | As | S | Cl | Hg | Sb | Bi | Ag | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 68.77 | 0.02 | 4.97 | 0.06 | 0.00 | 0.11 | 0.31 | 1.14 | 0.08 | 0.15 | 0.03 | 75.64 |
| **2** | 55.84 | 0.03 | 13.38 | 0.16 | 0.00 | 0.29 | 0.51 | 0.00 | 0.04 | 0.18 | 0.00 | 70.42 |
| **3** | 85.85 | 0.00 | 11.58 | 0.15 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.21 | 0.09 | 97.89 |
| **4** | 63.94 | 0.00 | 0.05 | 0.11 | 1.35 | 0.01 | 32.24 | 1.23 | 0.02 | 0.00 | 0.05 | 99.00 |
| **5** | 63.60 | 0.01 | 0.00 | 0.09 | 0.18 | 0.00 | 29.14 | 2.45 | 0.04 | 0.00 | 0.07 | 95.58 |
| **6** | 86.71 | 0.02 | 11.64 | 0.01 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.07 | 0.06 | 98.52 |
| **7** | 61.64 | 0.00 | 0.03 | 0.01 | 1.22 | 0.01 | 33.69 | 3.46 | 0.03 | 0.00 | 0.08 | 100.16 |
| **8** | 64.11 | 0.00 | 0.01 | 0.02 | 0.00 | 0.00 | 30.65 | 1.62 | 0.05 | 0.09 | 0.04 | 96.59 |
| **9** | 64.98 | 0.01 | 0.03 | 0.03 | 1.10 | 0.04 | 30.92 | 2.77 | 0.01 | 0.00 | 0.08 | 99.96 |
| **10** | 64.72 | 0.00 | 0.06 | 0.01 | 0.52 | 0.00 | 32.20 | 4.82 | 0.04 | 0.04 | 0.07 | 102.48 |
| **11** | 80.62 | 0.02 | 1.97 | 0.08 | 0.00 | 0.08 | 0.25 | 2.42 | 0.18 | 0.03 | 0.00 | 85.64 |
| **12** | 87.35 | 0.00 | 10.99 | 0.09 | 0.00 | 0.02 | 0.00 | 0.00 | 0.00 | 0.00 | 0.07 | 98.53 |
| **13** | 85.57 | 0.01 | 0.04 | 0.00 | 0.00 | 0.01 | 0.01 | 0.00 | 0.00 | 0.00 | 0.06 | 85.69 |
| **14** | 72.30 | 0.03 | 11.62 | 0.10 | 0.00 | 0.18 | 0.06 | 0.00 | 0.06 | 0.10 | 0.02 | 84.48 |
| **15** | 52.00 | 0.00 | 24.10 | 0.44 | 0.00 | 0.14 | 0.51 | 0.00 | 0.00 | 0.10 | 0.02 | 77.31 |
| **16** | 58.84 | 0.05 | 21.33 | 0.54 | 0.00 | 0.20 | 0.50 | 0.00 | 0.00 | 0.06 | 0.01 | 81.53 |
| **17** | 83.47 | 0.03 | 0.02 | 0.00 | 0.00 | 0.01 | 0.20 | 0.00 | 0.00 | 0.00 | 0.04 | 83.77 |
| **18** | 6.00 | 0.28 | 0.00 | 0.00 | 0.00 | 0.02 | 0.00 | 3.83 | 0.06 | 0.18 | 0.03 | 10.40 |
| **19** | 78.56 | 0.06 | 0.01 | 0.14 | 0.00 | 0.03 | 0.22 | 0.00 | 0.00 | 0.00 | 0.06 | 79.08 |
| **20** | 52.71 | 0.00 | 0.01 | 0.00 | 0.00 | 0.01 | 0.27 | 1.80 | 0.01 | 0.05 | 0.02 | 54.89 |
| **21** | 11.29 | 0.00 | 2.50 | 0.38 | 0.00 | 0.04 | 0.01 | 0.00 | 0.00 | 0.03 | 0.01 | 14.26 |
| **22** | 39.75 | 0.03 | 25.35 | 0.04 | 0.00 | 0.03 | 0.23 | 0.00 | 0.00 | 0.17 | 0.00 | 65.61 |
| **23** | 93.66 | 0.00 | 0.01 | 0.00 | 0.00 | 0.03 | 0.13 | 0.06 | 0.00 | 0.05 | 0.01 | 93.94 |
| **24** | 89.80 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.22 | 0.50 | 0.01 | 0.12 | 0.08 | 90.73 |

The results show that Cl is almost absent in the surface layers. Nevertheless, Cl was found in the metal. The ratio of Cu to Cl indicates that it is likely to be nantokite. SEI shows that it is softer than the surrounding matrix. Hg is present with chloride, with contents of 1.23-4.82%. The examined areas were damaged by the incident beam, with holes left due to the evaporation of Hg (Fig. 10). Arsenic was found with chloride as well, with content being up to 1.35%. Cl was detected in the corroded boundary of α grains as well. Cl penetrated to metal from the soil along the grain boundaries and reacted with Cu to form nantokite. Nantokite was sealed in the corroded passivated metal, and was not able to access to oxygen and water to form bronze disease. The presence of As and Hg assumes that they were brought into the metal with chloride ions. Hg was found in a few spots in corrosion area with contents being up to 3.83%. This suggests that Hg have probably been from the burial environment.

## SUMMARY

It is a binary alloy of Cu-Sn with an equi-axed structure. The best estimate of the original composition provided by EPMA combined with AAS data is : about 85-87% Cu and 12% Sn. Bronze disease was not found on the surface, although nantokite was detected in the metal. Hg was detected in the corrosion pits of nantokite. Redeposited Cu is present within cuprite and nantokite.

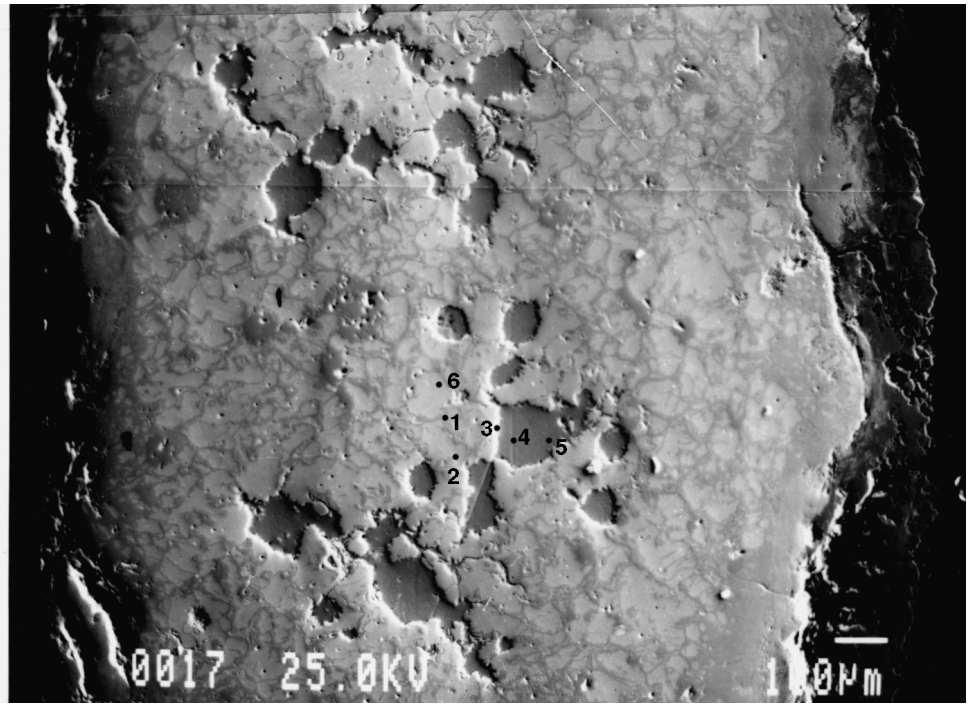



Fig. 8 BEI of metallographic section, showing EPMA points.

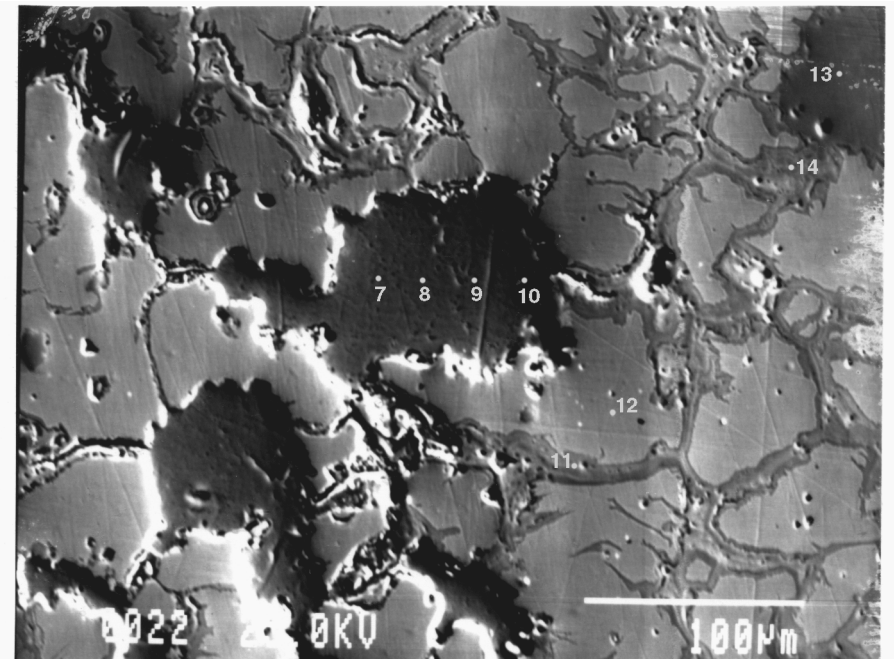



Fig. 9 SEI of corrosion pits, showing EPMA points.

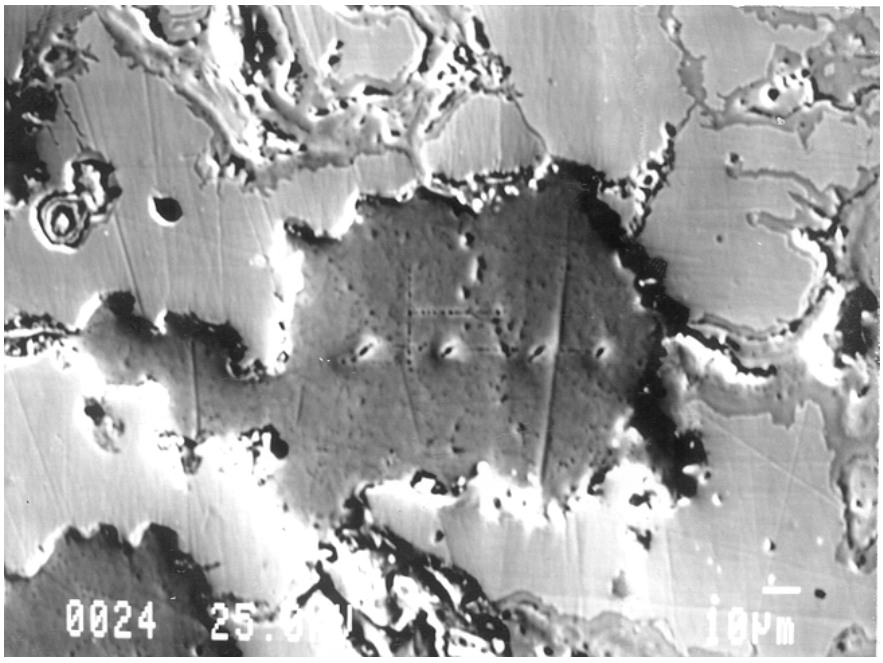



Fig. 10 SEI of corrosion pits, damaged by electron beams.

## GENERAL

**Object Number:** M6511:13
**Excavation Date:** 1988
**Origin:** Tianma-Qucun site

**Object:** weapon/*ge* spear
**Date:** Middle Western Zhou
**Fragment Weight:** 0.7 g
**Fragment size:** 11x8x (0.5-3.0) mm

**General description:**

This fragment has all sides broken. Corrosion index is 4. Holes in the cross section are filled with corrosion products (Fig. 1). The surface is covered with green and blue corrosion products and soil. No decoration is apparent.

## TECHNICAL STUDIES OF METAL

**Metallographic structure:**

The whole piece was mounted with cross section down for metallographic observation. The metallographic section (Fig. 2) nearly represents an entire cross section of the object: from centre to edge. The thickness varies from 0.5-3.0 mm. It has a dendritic structure with sulphide inclusions (Fig. 3). The presence of dendritic structure indicates that it was not worked. There is no difference in microstructure among different areas. It was probably just an object for burial rather than for practical purpose.

**Composition:**

**AAS:** too corroded for analysis.

**Microanalysis:**

SEM/EDS semi-quantitative analysis was carried out on the least corroded metal (400x), the result shows that it is a binary alloy of Cu-Sn. The total is low, so the Sn is over estimated. Cl is present in this sample.

| Cu | Sn | Cl | Si | S | Total |
|---|---|---|---|---|---|
| 56.3 | 23.7 | 3.4 | 0.2 | 0.5 | 84.9 |

**Microhardness:** 116Hv

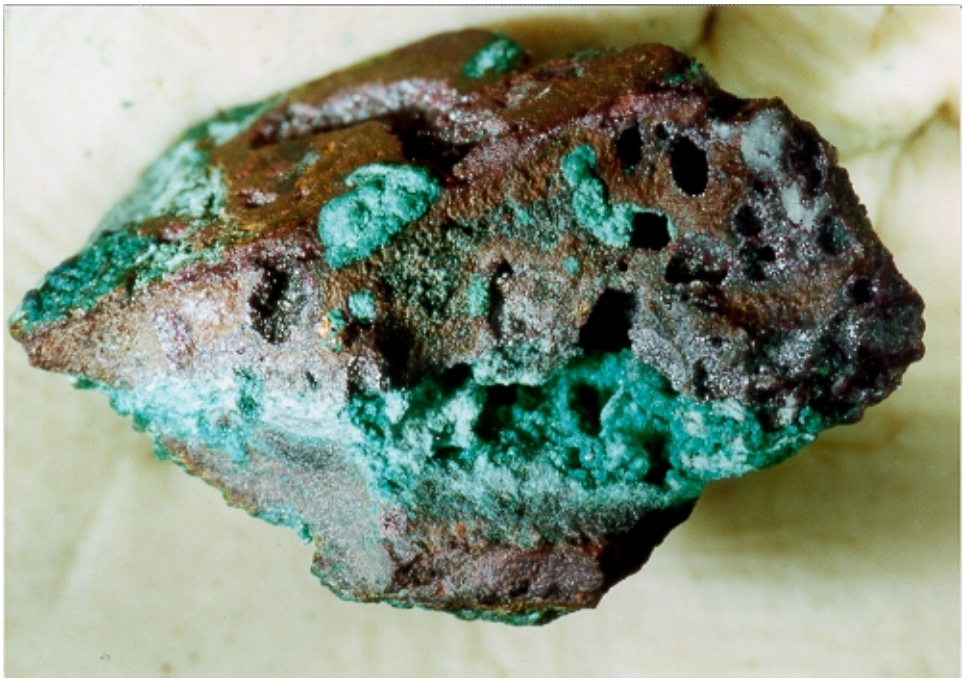


Fig. 1 General view of cross section of the fragment, showing holes filled with corrosion products.
Width of the image = 14 mm.

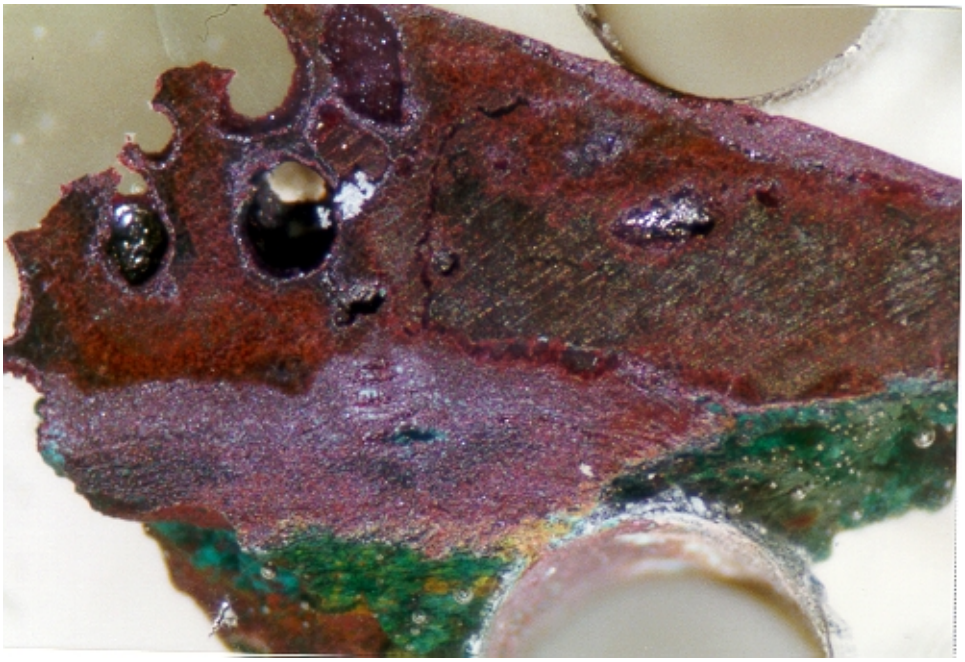


Fig. 2 The metallographic section.
Width of the image = 6 mm.

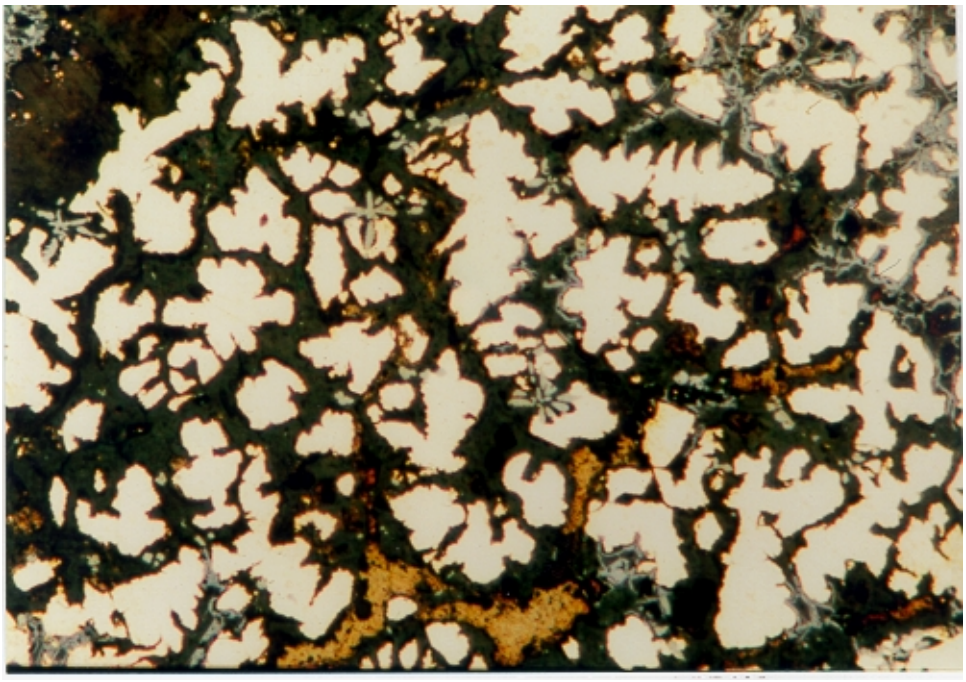


Fig. 3 Dendritic microstructure of the corroded metal.

BF. Width of the image = 0.5 mm.

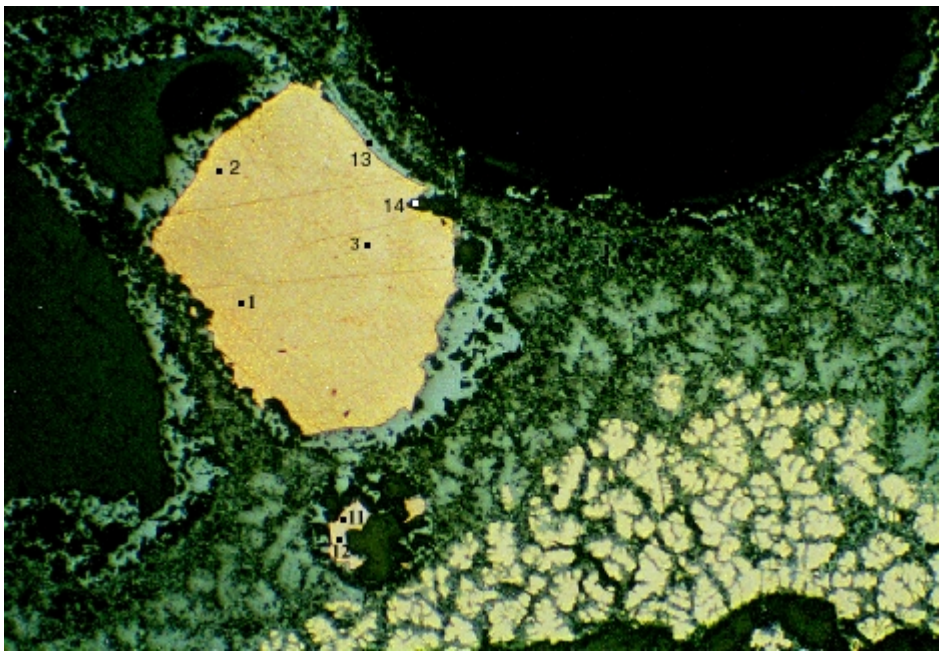



Fig. 4 Redeposited Cu in the corroded metal.

BF. Width of the image = 2mm.

## CORROSION

**XRD results:** not carried out.

**Metallographic observation:**

It is deeply corroded, with α phases being left in some areas. Redeposited Cu is seen in corrosion inside the metal (Fig. 3). An area of redeposited Cu (about 0.7mm$^2$) is seen near a big hole. Redeposited Cu is also seen in some holes (Fig. 4). The redeposited Cu does not show twin lines after etched. There is a stripe of corrosion, which was suspected to be nantokite (Fig. 5).

**Microanalysis:**

EPMA was carried out; the results are as follows (Figs. 4 & 6):

| Point | Description |
|---|---|
| **1, 2, 3, 11, 12, 14** | Redeposited Cu |
| **4, 5, 6** | Remnant α phase |
| **7, 8, 9** | Nantokite |
| **10** | Cassiterite with copper chloride |
| **13** | Cuprite |

| Point | Cu | Ni | Fe | Sn | Pb | As | Zn | Co | S | Cl | Sb | Bi | Ag | Hg | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 81.97 | 0.00 | 0.01 | 0.00 | 0.04 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.15 | 0.02 | 0.04 | 82.23 |
| **2** | 97.12 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.01 | 0.04 | 0.06 | 0.00 | 0.00 | 0.04 | 0.00 | 97.28 |
| **3** | 98.78 | 0.00 | 0.00 | 0.00 | 0.02 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.02 | 0.02 | 0.00 | 0.01 | 98.87 |
| **4** | 67.14 | 0.00 | 0.03 | 20.93 | 0.21 | 0.00 | 0.00 | 0.00 | 0.34 | 2.66 | 0.00 | 0.07 | 0.01 | 0.00 | 91.38 |
| **5** | 88.30 | 0.01 | 0.02 | 7.06 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.08 | 0.02 | 0.11 | 95.61 |
| **6** | 89.27 | 0.00 | 0.01 | 11.01 | 0.03 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.03 | 0.00 | 0.00 | 100.34 |
| **7** | 67.73 | 0.00 | 0.00 | 0.02 | 0.08 | 1.93 | 0.00 | 0.00 | 0.01 | 29.73 | 0.00 | 0.05 | 0.05 | 0.02 | 99.63 |
| **8** | 64.79 | 0.00 | 0.00 | 0.02 | 0.08 | 3.47 | 0.00 | 0.00 | 0.00 | 32.02 | 0.00 | 0.07 | 0.05 | 0.00 | 100.49 |
| **9** | 63.95 | 0.00 | 0.00 | 0.05 | 0.05 | 2.51 | 0.00 | 0.00 | 0.01 | 30.44 | 0.00 | 0.07 | 0.02 | 0.00 | 97.09 |
| **10** | 13.08 | 0.00 | 0.03 | 64.73 | 0.47 | 0.00 | 0.00 | 0.00 | 0.43 | 2.38 | 0.00 | 0.64 | 0.00 | 0.00 | 81.77 |
| **11** | 96.23 | 0.00 | 0.00 | 0.00 | 0.06 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.06 | 0.06 | 0.04 | 96.45 |
| **12** | 97.12 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.02 | 0.00 | 0.00 | 0.00 | 0.03 | 0.00 | 97.18 |
| **13** | 84.81 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.02 | 0.03 | 0.05 | 84.92 |
| **14** | 59.96 | 0.00 | 0.01 | 0.02 | 0.03 | 0.79 | 0.00 | 0.00 | 0.01 | 31.14 | 0.02 | 0.00 | 0.02 | 0.00 | 91.99 |

EPMA results do indicate the stripe of corrosion is nantokite. Arsenic seems like having correlation with Cl, this indicates that As was from environment brought in with $Cl^-$ rather than from the original metal composition with no As.

## SUMMARY

It is a binary alloy of Cu-Sn with sulphide inclusions. The original composition is not estimated because of corrosion. However, the tin content could be relatively high based on the dendritic structure. Redeposited Cu is present in the metal. Nantokite is detected in this sample. Bronze disease could have been present on the surface. Unfortunately there is no remnant sample for analysis.

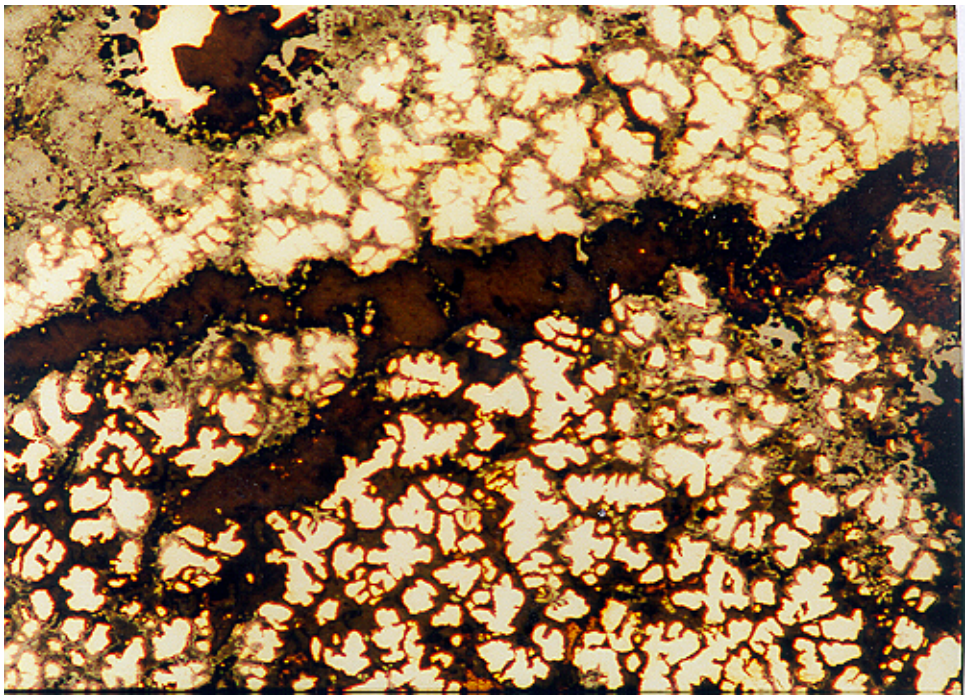


Fig. 5 Photomicrograph of nantokite stripe, confirmed by EPMA.
BF. Width of the image = 1mm.

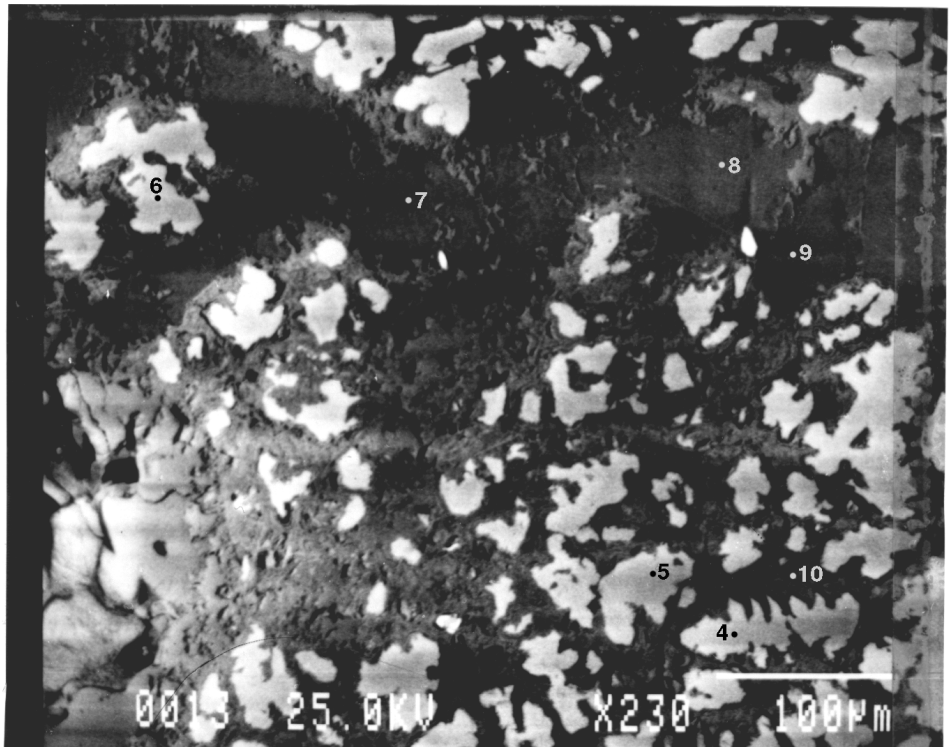



Fig. 6 SEI of corroded metal, showing EPMA points.

## GENERAL

**Object Number:** M5189:4
**Excavation Date:** 1982
**Origin:** Tianma-Qucun site

**Object:** vessel/*pan* (Fig. 1)
**Date:** Late Western Zhou
**Fragment Weight:** 1.8 g
**Fragment size:** 10x8x(2.4-3.4) mm

**General description:**

This fragment has all sides broken. Corrosion index is 5. There is a corrosion overburden and soil on the surface, comprising mainly of azurite, malachite based on their colours (Fig. 2) The broken cross section (Fig. 3) has 4 layers: yellowish, light blue, light green and blue (some places missed) from one surface (bottom) to the other (top). No decoration is apparent. This fragment was probably from the rim (either the top or the bottom) based on the fact that it has uneven thickness and no decoration.

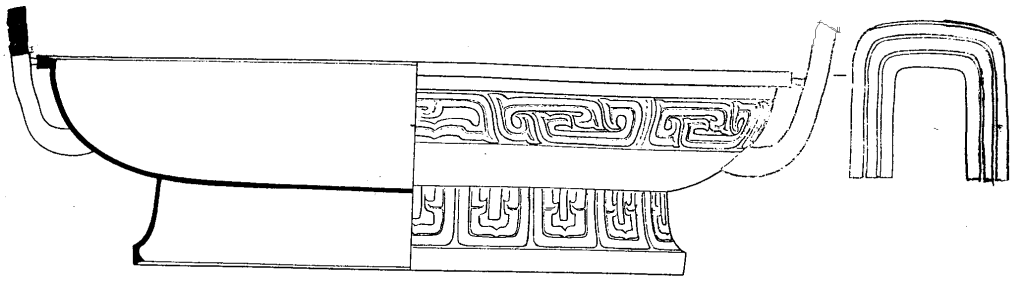


Fig. 1 The object

## TECHNICAL STUDIES OF METAL

**Metallographic structure:**

The whole piece was mounted for metallographic section. It is totally corroded. The original surfaces are preserved on one side. The estimated thickness is 2.4-3.4 mm as measured in the metallographic section. The corroded metal has a pseudormorphic dendritic structure.

**Composition:**

**AAS:** too corroded for analysis

**Microanalysis:**

See corrosion section

**Microhardness:** too corroded for measuring.

Fig. 2 General view of the fragment.
Width of the image = 11mm.

Fig. 3 View of the cross section of the fragment.
Width of the image = 11 mm.

## CORROSION

**XRD results:** not carried out.

**Metallographic observation:**

The metallographic section (Fig. 4), which corresponds to Fig. 3, shows 3 different layers. Light blue and blue layers in Fig. 3 seem to be the same under microscope. The yellowish layer on one surface is partially filled with powdery material; the blue layer is dense and mixed with cuprite; and the green layer is less dense.

The corrosion overburden is up to 1.3 mm thick on the surface where the blue layer is present. It is comprised of azurite, malachite, cuprite and soil based on their characteristic colours in the metallographic section. Fibrous malachite (or/and azurite) is also seen. Redeposited Cu is seen in cuprite in the corrosion overburden, copper sulphide is not observed in this piece. On the other surface, no corrosion overburden is present.

**Microanalysis:**

In order to find out the difference among these 3 layers of the corroded metal, EPMA linescan from A to B (Fig. 5) was carried out; the result (Fig. 6) shows that there is not much difference among 3 layers, except that Fe is richer in the yellowish corrosion layer (the outer layer), but Pb is a bit higher in the blue layer.

## SUMMARY

It is a ternary alloy of Cu-Sn-Pb based on EPMA data. It has a dendritic structure. The original composition is not estimated, because it is totally corroded.

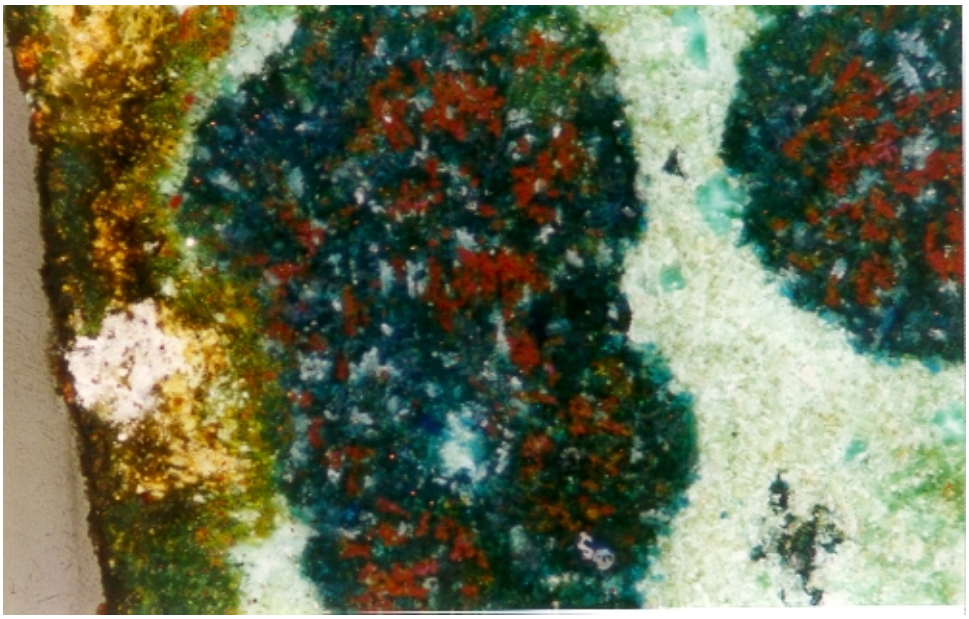


Fig. 4 Photomicrograph of corroded metal, showing 3 layers.

C/P. Width of the image = 2 mm.

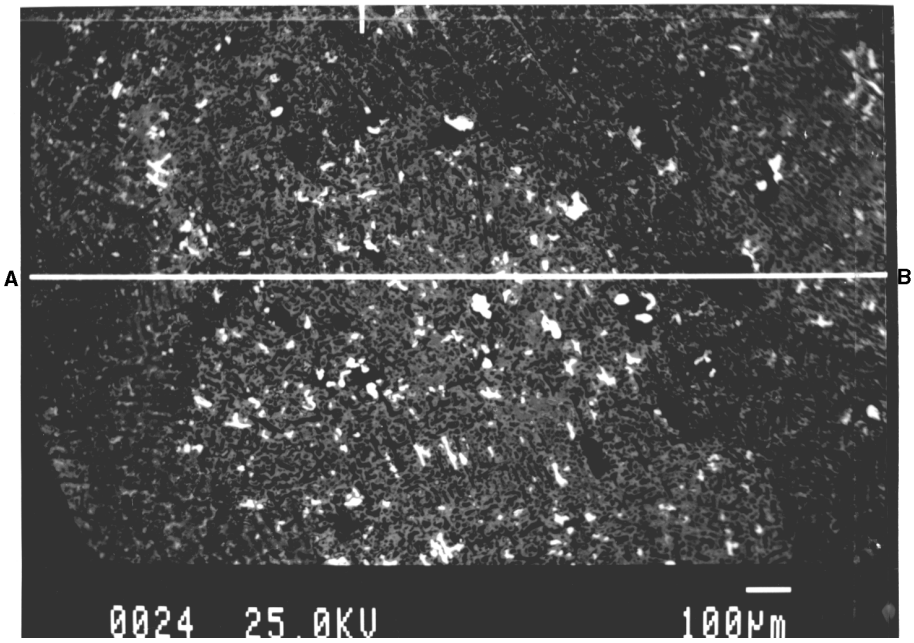



Fig. 5 BEI of corroded metal, showing EPMA linescan from A to B.

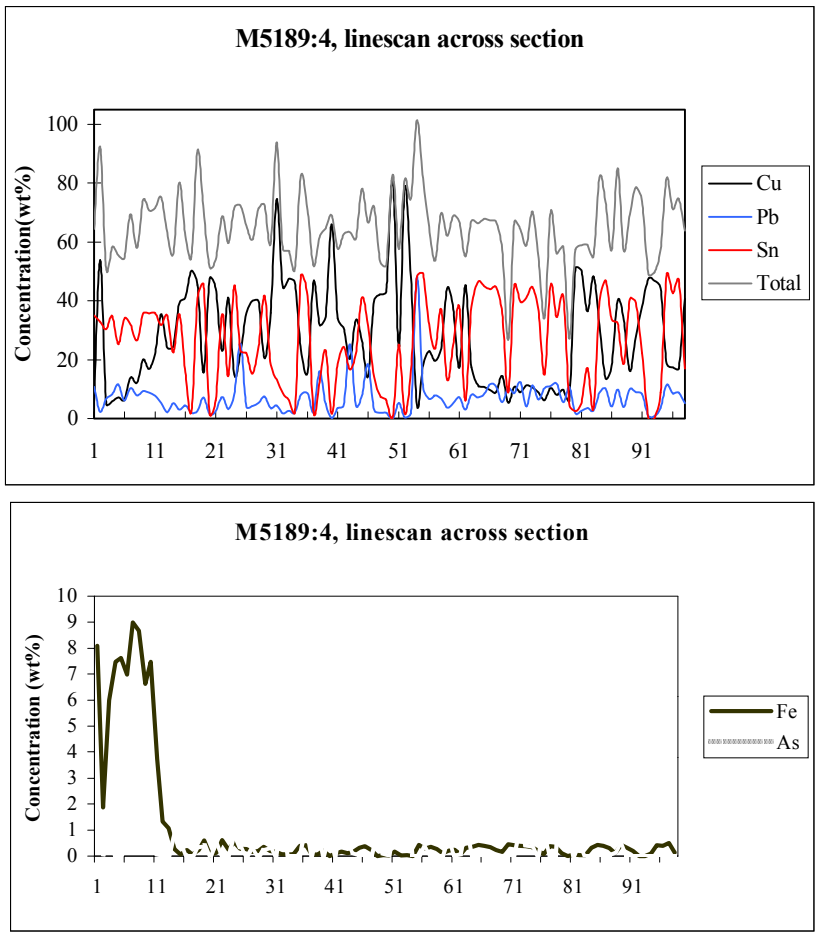



Fig. 6 EPMA linescan across section from A to B.

## GENERAL

**Object Number:** M5189:31
**Excavation Date:** 1982
**Origin:** Tianma-Qucun site

**Object:** horse fitting/snaffle bit
**Date:** Late Western Zhou
**Fragment Weight:** 0.8 g
**Fragment size:** 10x6x? mm

**General description:**

This fragment has all sides broken. Corrosion index is 5. The original surface is mainly covered with soil. The broken surface is covered with a thin layer of light green corrosion product with soil. No decoration is apparent.

## TECHNICAL STUDIES OF METAL

**Metallographic structure:**

A section cut through the full width of the fragment was taken for metallographic observation. It appears to be just a bit of original surface with corrosion overburden making up most of the sample. The original metal is thinner than 0.1 mm in this piece. δ phases are observed in the corroded metal. It seems to have a pseudomorphic dendritic structure (Fig. 1).

**Composition:**

**AAS:** too corroded for analysis.

**Microanalysis:**

SEM/EDS semi-quantitative analysis was carried out on the corroded metal (200x). The result suggests that it was a ternary alloy of Cu-Sn-Pb.

| Cu | Sn | Pb | Fe | Total |
|---|---|---|---|---|
| 18.0 | 10.5 | 16.5 | 0.6 | 45.6 |

**Microhardness:** too corroded for measuring.

## CORROSION

### XRD results:

Surface sample: mainly malachite, antlerite, quartz, with presence of azurite, brochantite, cuprite, β-copper sulphide ($Cu_2S$) and scotlandite.

### Metallographic observation:

It is totally corroded. The corrosion overburden is up to 3.2 mm thick, comprised of copper sulphide, malachite, and azurite based on their characteristic colours in the metallographic section (Fig. 2). Clusters (Fig. 3) and fibrous copper carbonate are also present. Cuprite is rarely seen. The presence of copper sulphides and sulphates are confirmed by XRD.

### Microanalysis:

EPMA was carried out on both the corroded metal (Fig. 1) and the corrosion overburden (Fig. 4); the results are as follows:

| Point | Description |
|---|---|
| **1, 4, 6** | Porous corrosion products |
| **2, 3** | Corrosion products of lead |
| **5** | Corroded α phase |
| **7** | Copper carbonate |
| **8** | Lead oxide or carbonate |
| **9** | Lead sulphide |

| Point | Cu | Fe | Pb | As | S | Cl | Ag | Sb | Bi | Hg | Si | P | Al | Sn | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 31.89 | 0.22 | 0.72 | 0.00 | 0.00 | 0.00 | 0.00 | 0.05 | 0.00 | 0.00 | 1.08 | 0.60 | 0.67 | 0.00 | 35.23 |
| **2** | 0.85 | 0.13 | 86.07 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.05 | 0.40 | 87.50 |
| **3** | 0.57 | 0.07 | 79.70 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.03 | 80.37 |
| **4** | 2.35 | 0.15 | 30.61 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.04 | 0.00 | 0.14 | 2.98 | 36.28 |
| **5** | 36.05 | 1.49 | 9.24 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.45 | 0.00 | 0.44 | 0.25 | 0.00 | 20.16 | 68.09 |
| **6** | 0.99 | 0.37 | 19.48 | 0.00 | 0.00 | 0.00 | 0.04 | 0.00 | 0.35 | 0.00 | 0.80 | 0.16 | 0.81 | 10.40 | 33.39 |
| **7** | 53.29 | 0.00 | 2.10 | 0.00 | 0.76 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.24 | 0.04 | 0.00 | 56.42 |
| **8** | 1.90 | 0.15 | 82.45 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.05 | 0.00 | 0.09 | 84.64 |
| **9** | 78.30 | 0.11 | 1.05 | 0.46 | 16.13 | 0.00 | 0.13 | 0.00 | 0.01 | 0.00 | 0.00 | 0.51 | 0.00 | 0.00 | 96.69 |

Microprobe colour maps (Fig. 5) were carried out on the surface, which show a very clear interface between the corrosion and the metal.

## SUMMARY

It is a ternary alloy of Cu-Sn-Pb with high contents of Pb. The original composition in not estimated, because it is totally corroded. It seems to have a dendritic structure. Cerussite, often observed in the corrosion of high leaded bronzes, is not seen in this sample. This was probably due to presence of sulphides in the corrosion.

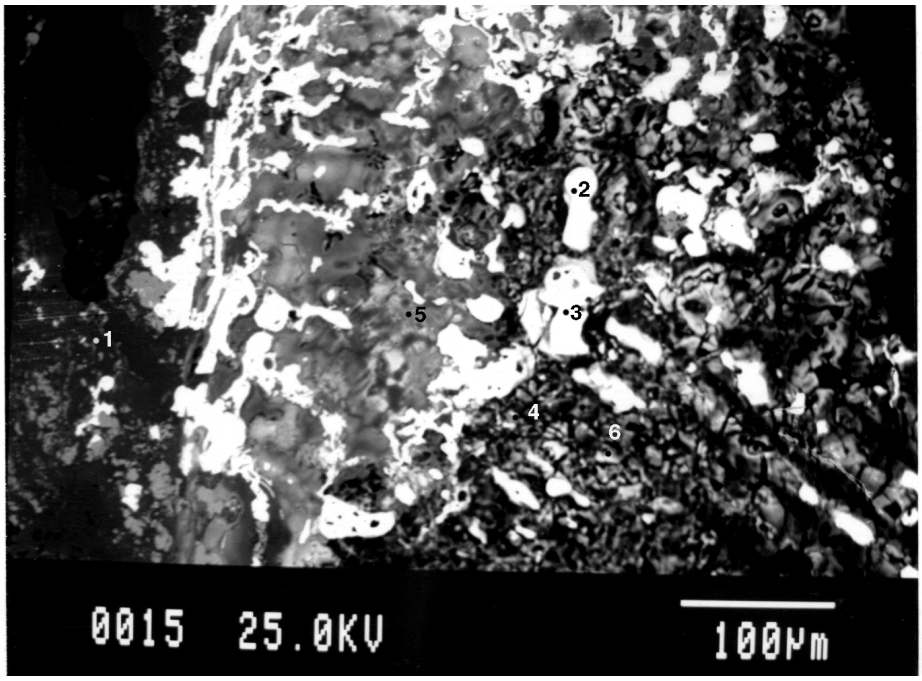



Fig. 1 BEI of corroded metal, showing EPMA points.

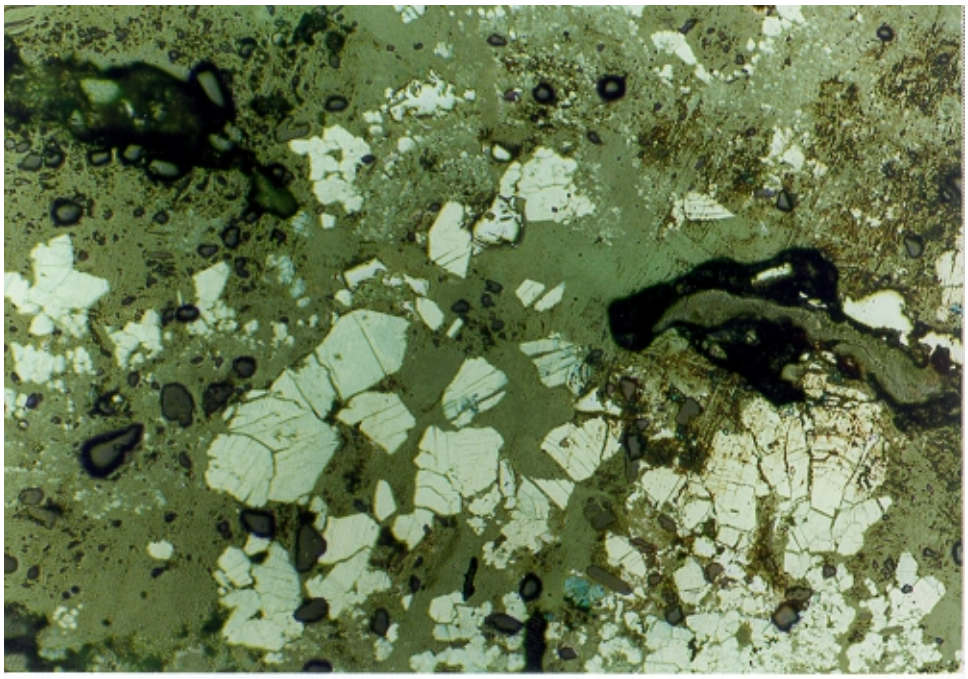


Fig. 2 Photomicrograph of copper sulphides in corrosion overburden.
BF. Width of the image = 0.7 mm.

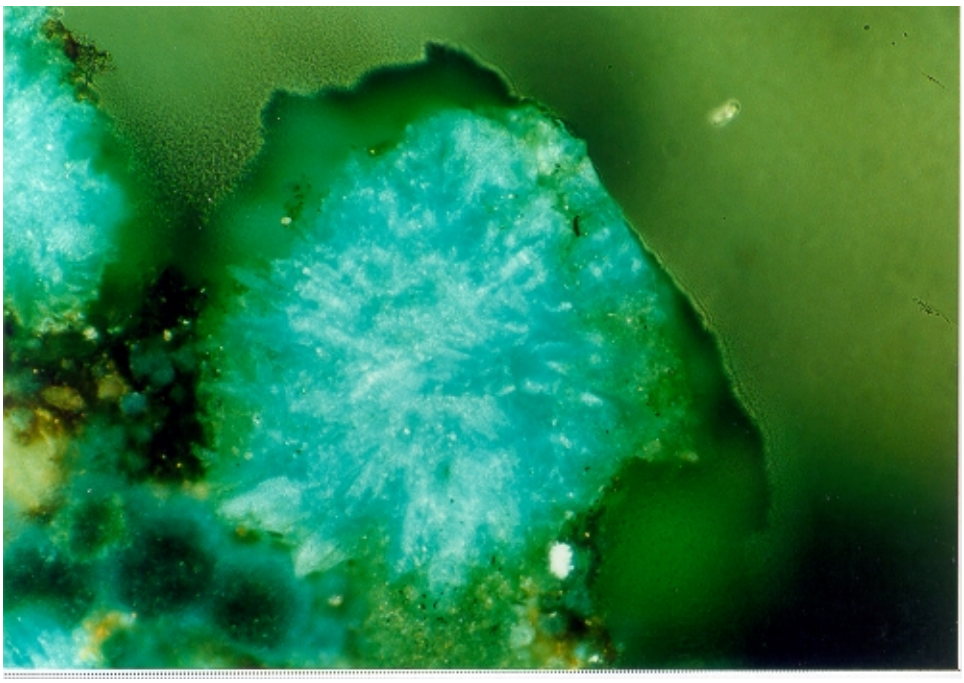


Fig. 3 Photomicrograph of cluster copper carbonate.
C/P. Width of the image = 0.7 mm.

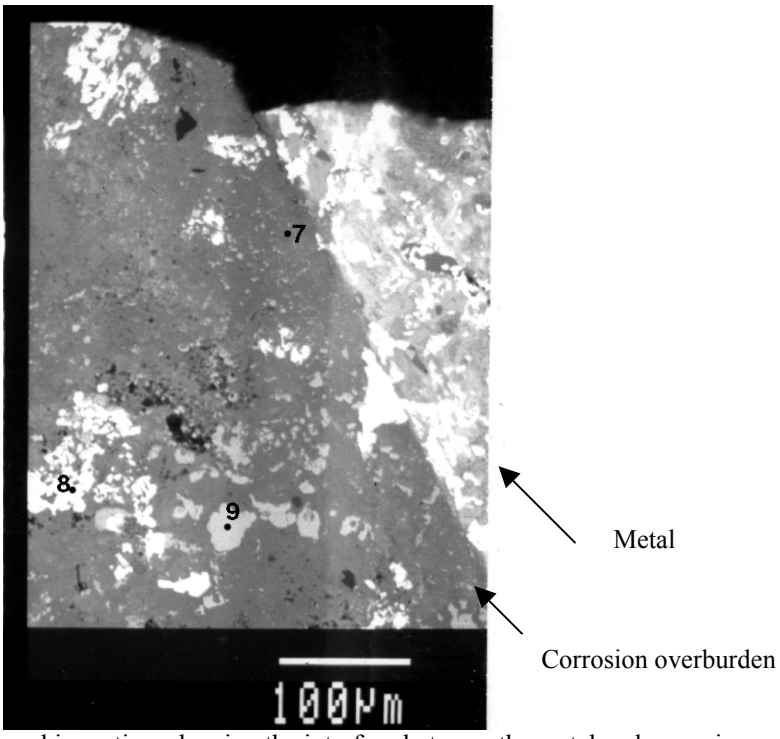



Fig. 4 BEI of metallographic section, showing the interface between the metal and corrosion overburden. EPMA points are also shown.

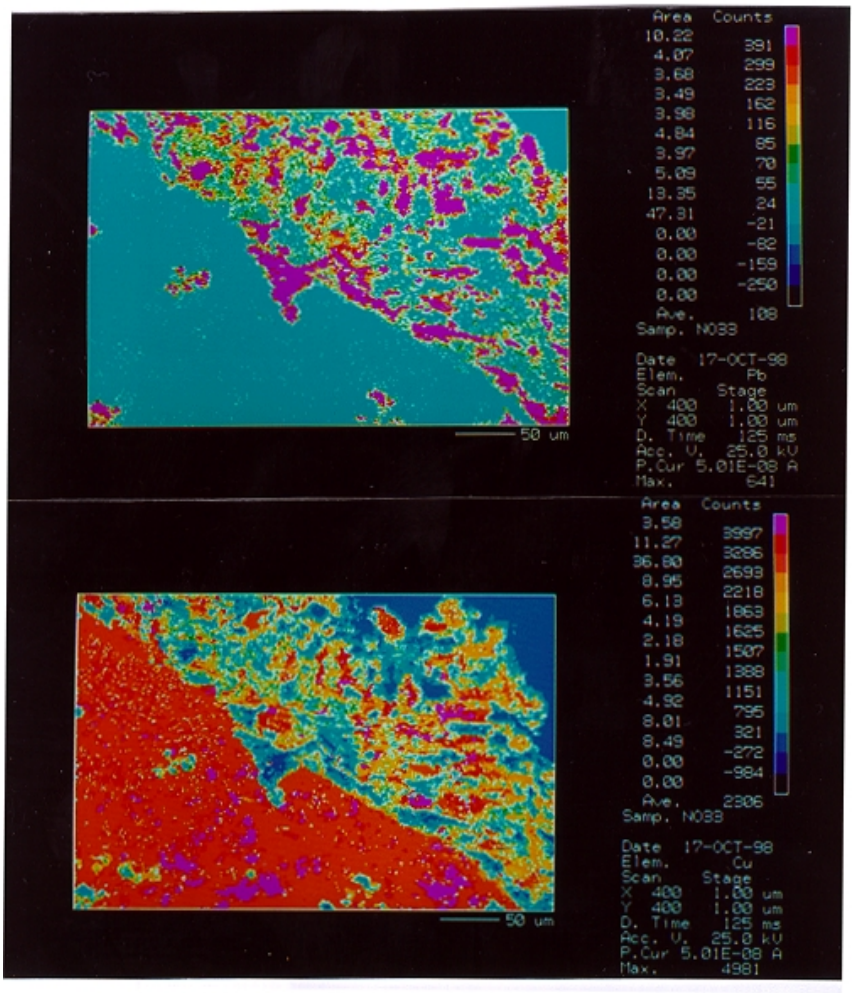



Fig. 5 EPMA colour maps of Fig. 4

## GENERAL

**Object Number:** M5189:33
**Excavation Date:** 1982
**Origin:** Tianma-Qucun site

**Object:** horse fitting/snaffle bit
**Date:** Late Western Zhou
**Fragment Weight:** 0.9 g
**Fragment size:** 5x4x1.4 mm

**General description:**

This small fragment has all sides broken. Corrosion index is 4. There is a corrosion overburden on the surface, including mainly light green and green corrosion products. Black corrosion products are also observed. No decoration is apparent.

## TECHNICAL STUDIES OF METAL

**Metallographic structure:**

The whole piece was mounted for metallographic section. Only a small area of metal is preserved (Fig. 1). The original surfaces can be seen. The estimated thickness is 1.4 mm as measured in the metallographic section. Microstructure of uncorroded metal (Fig. 2) indicates that it is a high lead object. The content of Sn must be low, because δ phase is not seen at all.

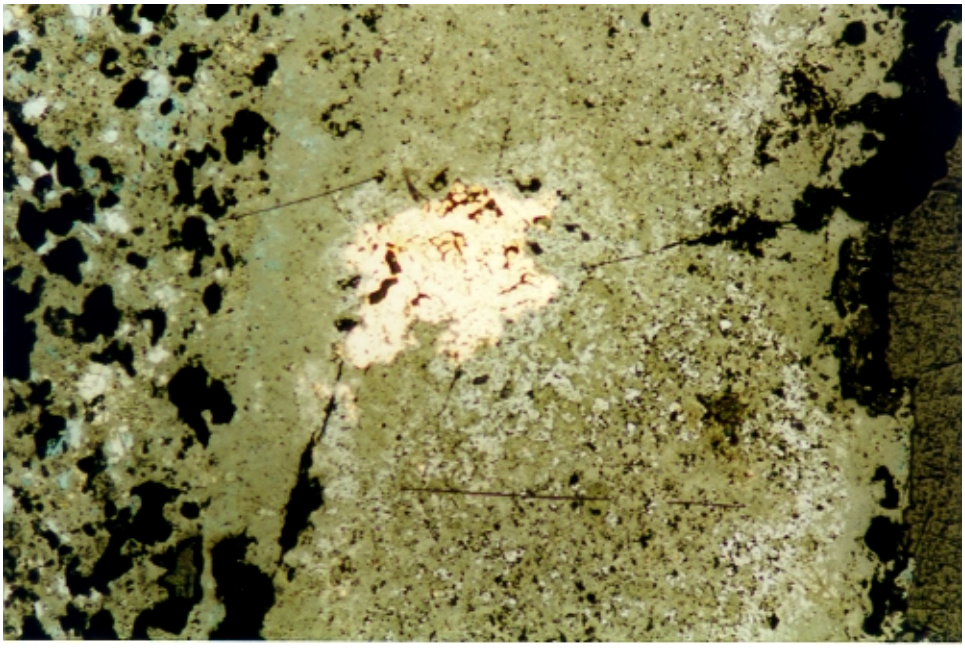


Fig. 1 Photomicrograph of the whole section, showing remnant of metal.
BF. Width of the image = 2 mm.

## Composition:

**AAS:** too corroded for analysis.

**Microanalysis:**

SEM/EDS semi-quantitative analysis was carried out on the uncorroded metal (300x), the results show that it is a ternary alloy of Cu-Sn-Pb with high Pb, and low Sn contents.

| Cu | Sn | Pb | Total |
|---|---|---|---|
| 65.8 | 4.0 | 22.6 | 92.4 |

**Microhardness:** 65.2Hv

## CORROSION

**XRD results:** not carried out.

### Metallographic observation:

Most of the metal has been corroded and converted to cuprite and cerussite (Fig. 3) based on their characteristic colours in the metallographic section. Corrosion overburden is up to 1.3 mm on one surface, while 0.4 mm on the other. Copper sulphides are present in the corrosion overburden (Fig. 1). Redeposited Cu is seen in cuprite in both corroded metal and corrosion overburden.

### Microanalysis:

EPMA was carried out on the remnant metal (Fig. 2); the results are as follows:

| Point | Cu | Fe | Pb | As | S | Cl | Ag | Sb | Bi | Hg | Si | P | Al | Sn | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 47.16 | 0.00 | 48.16 | 0.00 | 0.00 | 0.00 | 0.20 | 0.00 | 0.00 | 0.00 | 0.00 | 0.31 | 0.00 | 4.10 | 99.93 |
| 2 | 6.41 | 0.07 | 92.23 | 0.00 | 0.00 | 0.00 | 0.64 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.15 | 99.51 |
| 3 | 94.38 | 0.00 | 0.09 | 0.00 | 0.00 | 0.00 | 0.04 | 0.00 | 0.07 | 0.00 | 0.00 | 0.73 | 0.00 | 2.12 | 97.44 |
| 4 | 95.12 | 0.01 | 0.33 | 0.00 | 0.00 | 0.00 | 0.12 | 0.00 | 0.07 | 0.00 | 0.00 | 0.75 | 0.00 | 2.25 | 98.64 |
| 5 | 89.15 | 0.00 | 0.14 | 0.00 | 0.00 | 0.00 | 0.24 | 0.00 | 0.04 | 0.00 | 0.00 | 0.57 | 0.00 | 7.83 | 97.96 |
| 6 | 91.01 | 0.00 | 0.25 | 0.00 | 0.02 | 0.00 | 0.10 | 0.00 | 0.00 | 0.00 | 0.00 | 0.59 | 0.00 | 5.31 | 97.27 |
| 7 | 5.67 | 0.04 | 75.16 | 0.00 | 2.24 | 0.18 | 0.00 | 0.00 | 0.33 | 0.00 | 0.00 | 0.00 | 0.00 | 0.20 | 83.81 |
| 8 | 67.26 | 0.00 | 1.51 | 0.00 | 0.06 | 0.31 | 0.01 | 0.00 | 0.00 | 0.00 | 0.01 | 0.42 | 0.00 | 4.61 | 74.20 |
| 9 | 67.28 | 0.00 | 5.41 | 0.00 | 0.19 | 0.48 | 0.17 | 0.00 | 0.00 | 0.00 | 0.44 | 0.42 | 0.01 | 9.42 | 83.83 |
| 10 | 2.42 | 0.04 | 64.55 | 0.00 | 7.66 | 0.21 | 0.09 | 0.02 | 0.00 | 0.00 | 0.00 | 0.02 | 0.00 | 1.12 | 76.12 |
| 11 | 4.87 | 0.02 | 77.60 | 0.00 | 1.44 | 0.04 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.02 | 0.01 | 0.06 | 84.05 |
| 12 | 38.70 | 0.06 | 24.41 | 0.00 | 0.38 | 0.04 | 0.00 | 0.00 | 0.17 | 0.00 | 0.00 | 0.20 | 0.02 | 3.74 | 67.81 |
| 13 | 6.67 | 0.01 | 18.67 | 0.00 | 0.17 | 2.75 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.06 | 0.00 | 0.07 | 28.38 |
| 14 | 11.25 | 0.06 | 45.44 | 0.00 | 0.00 | 7.46 | 0.69 | 0.00 | 0.10 | 0.00 | 0.00 | 0.00 | 0.00 | 2.00 | 67.00 |
| 15 | 16.22 | 0.03 | 41.03 | 0.00 | 0.05 | 7.78 | 0.14 | 0.00 | 0.00 | 0.00 | 0.00 | 0.07 | 0.00 | 0.27 | 65.58 |

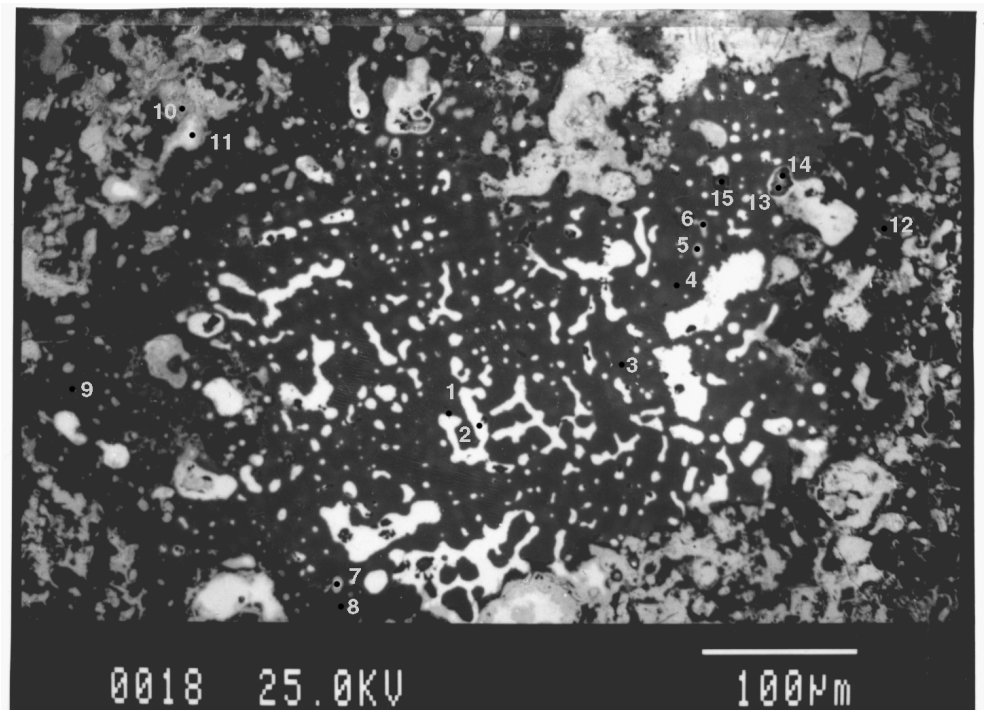



Fig. 2 BEI of metal, showing EPMA points.

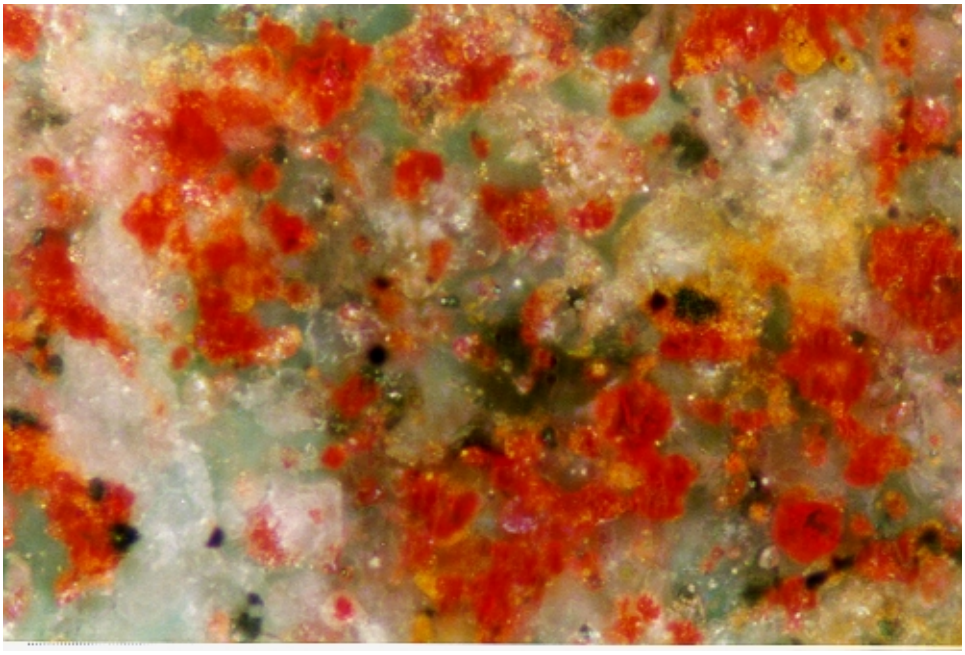


Fig. 3 Photomicrograph of the corroded metal, showing cuprite and cerussite (white materials). C/P. Width of the image = 0.2 mm.

| Point | Description |
|---|---|
| **1, 2** | Lead |
| **3, 4** | α phase |
| **5, 6** | Lighter than α phase in BEI, which contains higher Sn |
| **7** | Similar to 5 & 6, but rich in Pb |
| **8, 9, 12** | Corroded α phase |
| **10, 11** | Corroded lead |
| **13, 14, 15** | Lead attacked by $Cl^-$ |

Above data show that some Pb globules were corroded and partially converted to chlorides. However, bronze disease was not detected on the surface by SEM qualitative analysis.

## SUMMARY

It is a ternary alloy of Cu-Sn-Pb. The best estimate of bulk composition determined by SEM/EDS is 66% Cu, 4% Sn, and 23% Pb. It is likely an equi-axed structure. It is severely corroded. Some Pb globules are partially attacked by $Cl^-$.

## GENERAL

**Object Number:** unknown
**Excavation Date:** 1979
**Origin:** Shijiayuan site, Chunhua, Shaanxi

**Object:** mirror
**Date:** Early Western Zhou
**Fragment Weight:** 0.8 g
**Fragment size:** 10x7x1.2 mm

**General description:**

This fragment has all sides broken. Corrosion overburden is 5. There is a corrosion overburden on the surface, including light green and green corrosion products and soil (Fig. 1) The cross section is of two layers - blackish and reddish colours (Fig. 2). No decoration is apparent.

## TECHNICAL STUDIES OF METAL

**Metallographic structure:**

The whole piece was mounted with the cross section facing down for metallographic observation (Fig. 2). The original surfaces are well preserved although the metal is totally corroded. The estimated thickness is 1.2 mm as measured in the metallographic section. Two layers of different colours are clearly seen (Fig. 2). These two layers do not show difference in microstructure except that the blackish part is more porous (Fig. 3). This can clearly be seen in backscattered electron image (Fig. 4). It has a dendritic structure. The estimated dendritic arm spacing is 0.030 mm.

**Composition:**

**AAS:** too corroded for analysis.

**Microanalysis:**

SEM/EDS semi-quantitative analysis was carried out on the corroded metal (200x), the result shows that it is a ternary alloy of Cu-Sn-Pb. The tin content is over estimated, because the total is low (due to corrosion).

| Cu | Sn | Pb | Fe | Cl | Total |
|---|---|---|---|---|---|
| 50.5 | 27.1 | 3.6 | 0.2 | 0.1 | 81.5 |

**Microhardness:** too corroded for measuring

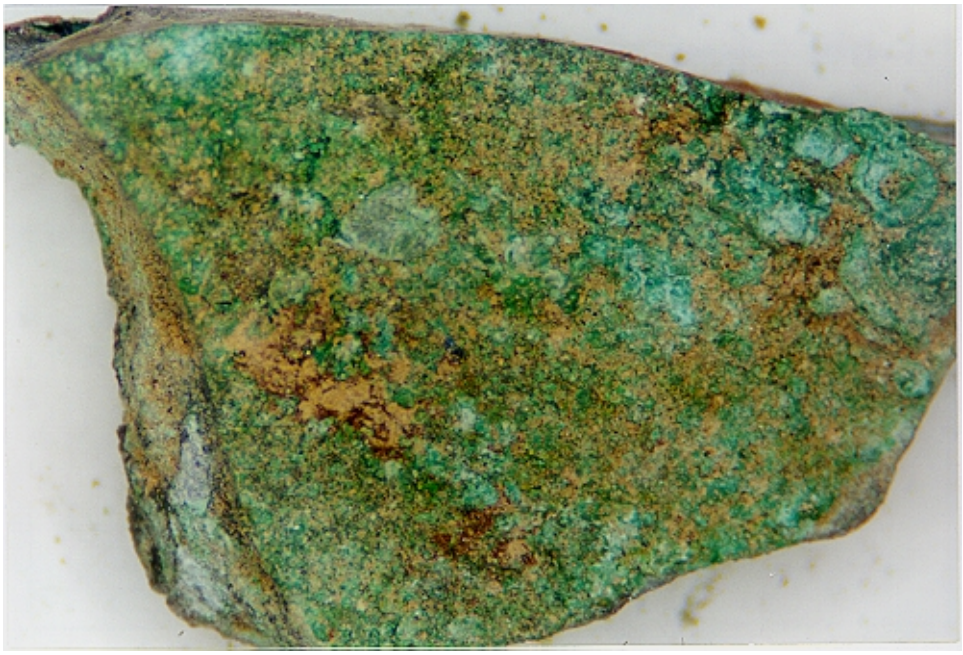


Fig. 1 General view of a surface of the fragment.
Width of the image = 7 mm.

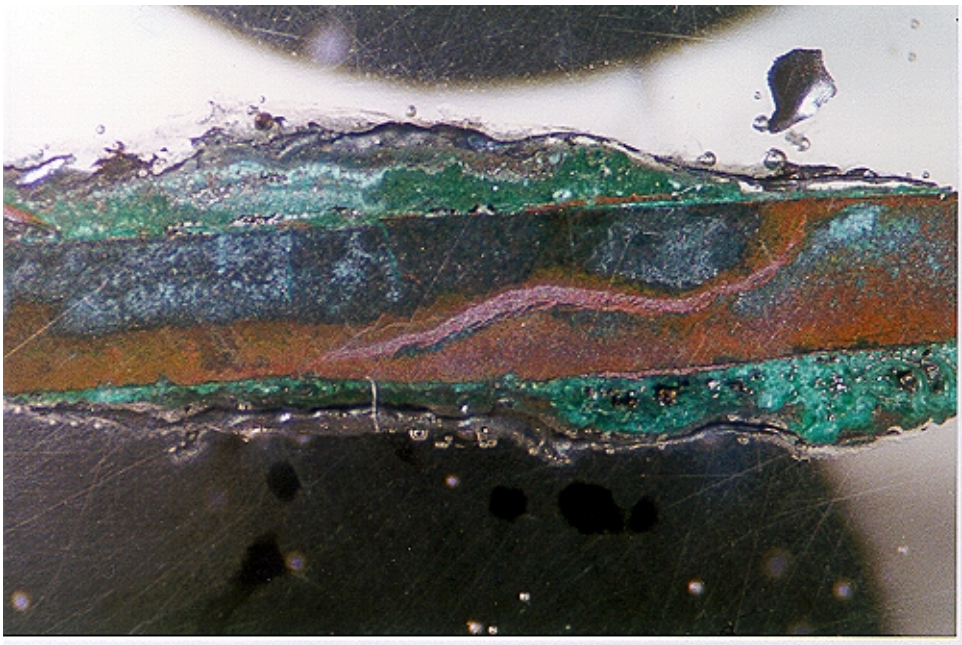


Fig. 2 Metallographic section, showing two layers of different colours within the original dimensions.
Width of the image = 7 mm.

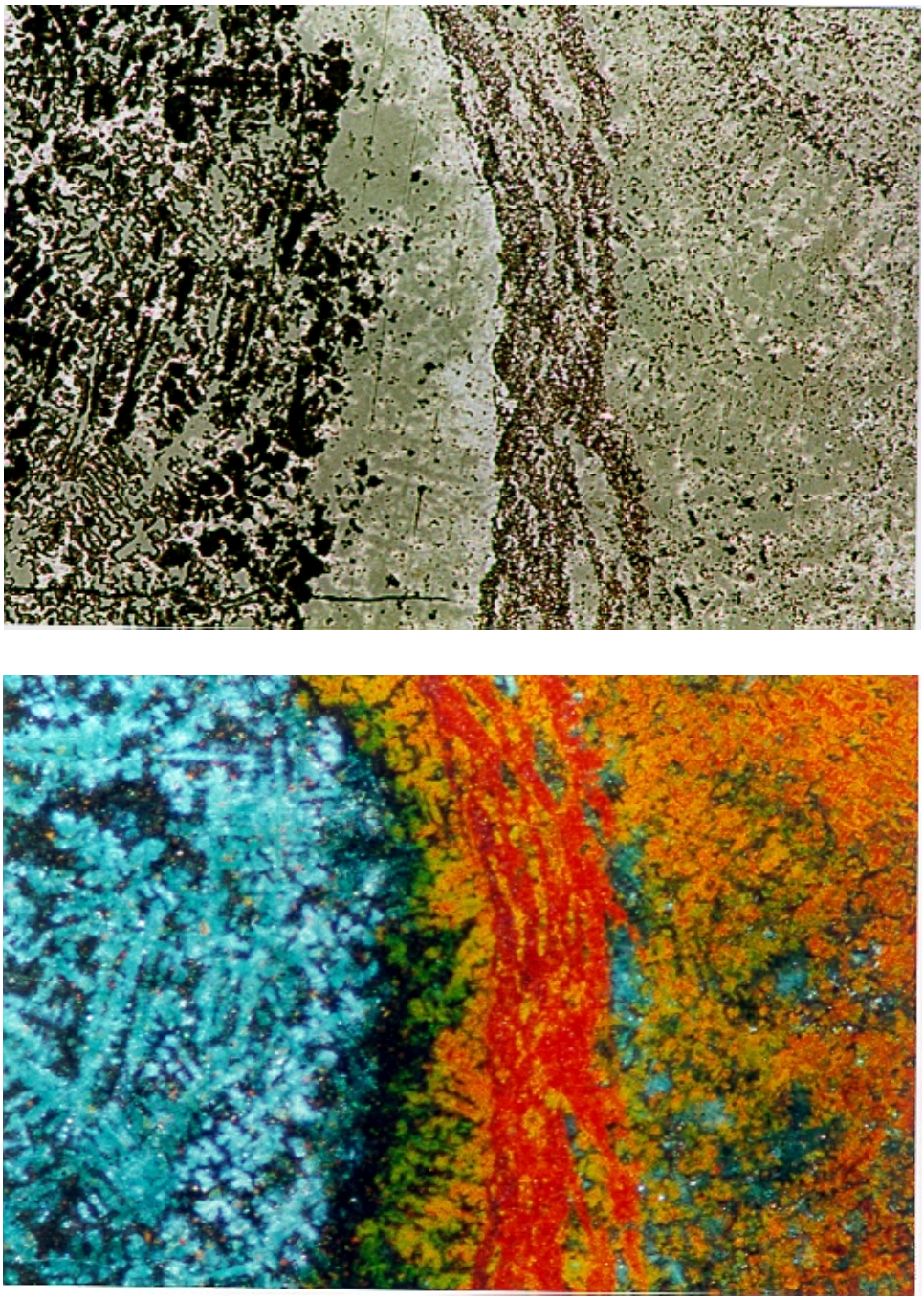


Fig. 3 Photomicrograph of corroded metal, showing the two layers of different colours. Width of the image = 1mm. Top: BF; Bottom: C/P.

## CORROSION

### XRD results:

Surface sample: malachite, $FeSO_3$, $SiO_2$, $SnO_2$, $CaAl_2(CO_3)_2(OH)_2.3H_2O$. Except malachite and cassiterite, other minerals are likely from soil.

### Metallographic observation:

It seems like that the reddish layer is mainly cuprite and cassiterite, the blackish layer is mainly copper carbonate and cassiterite based on their colours. The corrosion overburden is mainly comprised of malachite based on its colour.

### Microanalysis:

EPMA was carried out on the corroded metal; the results are shown below (Fig. 4). Points 1 – 3 are in the reddish layer; points 4 – 8 are in the blackish layer.

| Point | Cu | Fe | Au | Ni | Sn | Pb | Zn | Ag | Hg | As | Sb | Bi | Co | S | Cl | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 33.62 | 0.08 | 0.00 | 0.00 | 24.64 | 2.89 | 0.00 | 0.08 | 0.00 | 0.02 | 0.00 | 0.31 | 0.01 | 0.08 | 0.06 | 61.78 |
| **2** | 58.78 | 0.09 | 0.00 | 0.00 | 15.19 | 2.52 | 0.00 | 0.52 | 0.01 | 0.00 | 0.00 | 0.00 | 0.01 | 3.79 | 0.67 | 81.59 |
| **3** | 35.51 | 0.23 | 0.01 | 0.01 | 38.57 | 4.13 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.20 | 0.31 | 78.98 |
| **4** | 38.98 | 0.15 | 0.01 | 0.00 | 25.83 | 3.25 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.06 | 0.01 | 0.02 | 0.01 | 68.30 |
| **5** | 29.18 | 0.15 | 0.00 | 0.00 | 28.85 | 3.12 | 0.00 | 0.02 | 0.00 | 0.04 | 0.00 | 0.07 | 0.02 | 0.03 | 0.03 | 61.49 |
| **6** | 62.84 | 0.03 | 0.00 | 0.00 | 1.50 | 1.42 | 0.00 | 0.02 | 0.00 | 0.00 | 0.00 | 0.35 | 0.00 | 0.11 | 0.00 | 66.27 |
| **7** | 20.17 | 4.62 | 0.00 | 0.01 | 37.56 | 5.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.08 | 0.01 | 0.11 | 0.03 | 67.59 |
| **8** | 39.02 | 0.03 | 0.03 | 0.14 | 37.92 | 2.07 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.01 | 0.01 | 0.05 | 0.00 | 79.28 |

EPMA was also carried out on the corrosion to check bronze disease, the results show that bronze disease is absent.

## SUMMARY

It is a ternary alloy of Cu-Sn –Pb with relatively high content of Sn. It has a dendritic structure. It is totally corroded. Artificial patina was not detected. Bronze disease is absent.

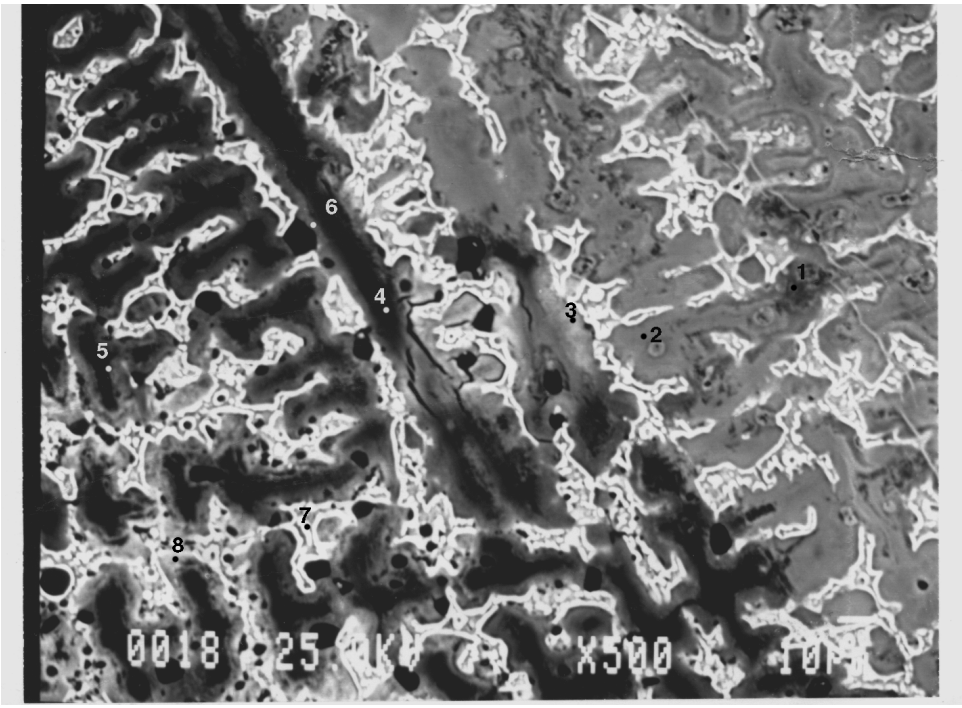



Fig. 4 BEI of corroded metal, showing EPMA points.

## GENERAL

**Object Number:** yoke 1

**Excavation Date:** 1998

**Origin:** No1 chariot pit at Xujiahutong, in east of Zhaochen site, Fufeng, Shaanxi

**Object:** horse fitting/ yoke

**Date:** Middle or late Western Zhou

**Fragment Weight:** 0.7 g

**Fragment size:** 11x8x1.1 mm

**General description:**

This fragment has all sides broken. Corrosion index is 3. There is a corrosion overburden on the surface, including nodular malachite, soil and cuprite underneath. No decoration is apparent.

## TECHNICAL STUDIES OF METAL

**Metallographic structure:**

The whole piece was mounted with the cross section facing down for metallographic observation. The original surfaces are well preserved. The estimated thickness is 1.1 mm as measured in the metallographic section. The hole (about 500 μm) in centre (Fig. 1) could be cast defect. It looks like dendritic structure, since a cored structure and eutectoid are present (Fig. 2). Sulphide inclusions are present in the metal.

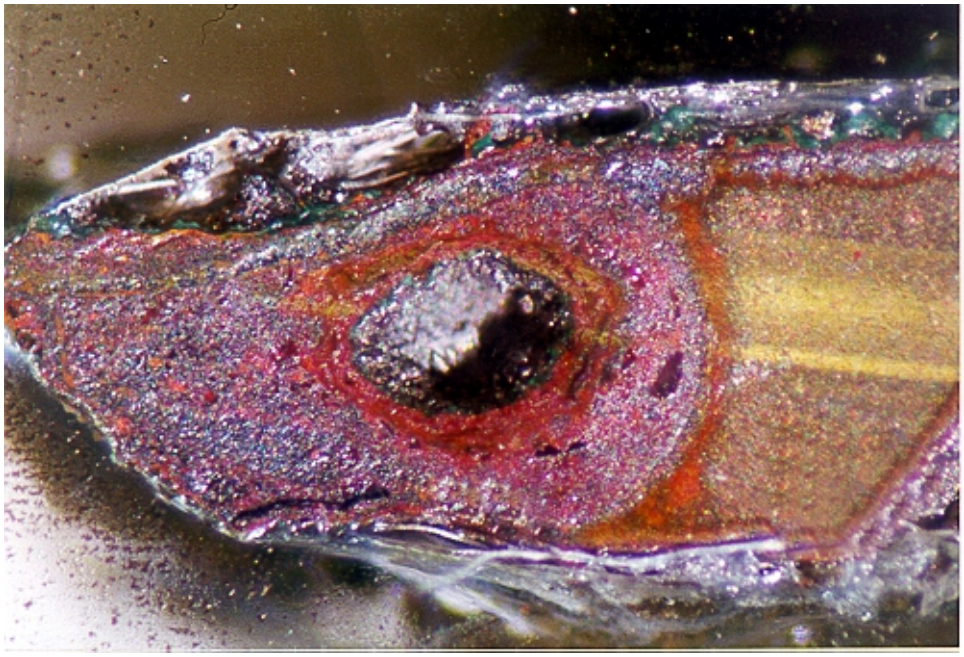


Fig. 1 A big hole in centre of metallographic section. C/P. Width of the image = 2 mm.

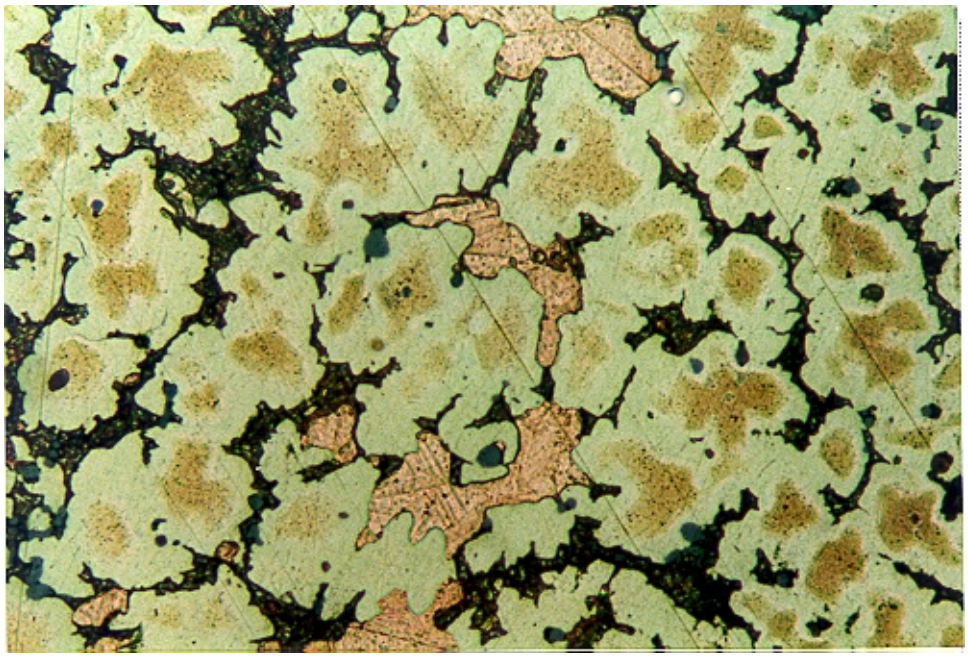


Fig. 2 Microstructure of corroded metal, showing cored structure and eutectoid.
BF. Width of the image = 0.2 mm.

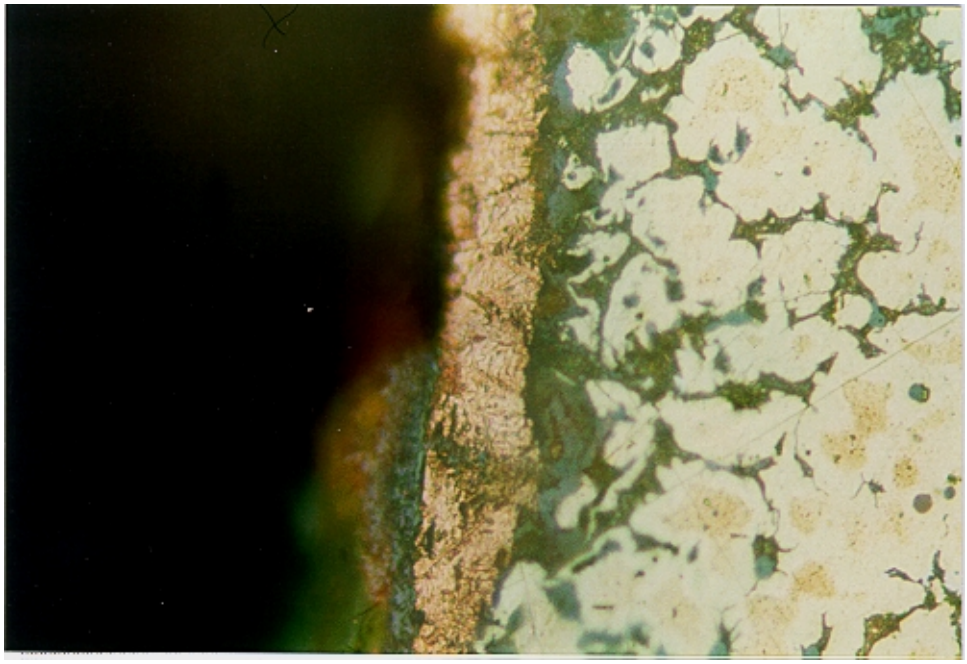


Fig. 3 Photomicrograph of a band of redeposited Cu on a surface.
BF. Width of the image = 0.2 mm.

**Composition:**

**AAS:** too corroded for analysis.

**Microanalysis:**

SEM/EDS semi-quantitative analysis was carried out on the least corroded metal (300x), the result shows that it is a binary alloy of Cu-Sn.

| Cu | Sn | Fe | Total |
|---|---|---|---|
| 75.6 | 15.6 | 1.1 | 92.3 |

**Microhardness:** 120Hv

**CORROSION**

**XRD results:**

Surface sample: malachite, quartz, cuprite.

**Metallographic observation:**

Corrosion went through the metal, most δ phases have corroded (Fig. 2). Redeposited Cu is seen in the areas where δ phases have gone. These Cu particles could be the result of destannification, because they are exactly in the place where δ phases were (Fig. 2). A band of redeposited Cu is seen on one surface (Fig. 3).

The hole mentioned above is of a banded structure; it appears red and black in colour at the edge but green inside the hole in cross polarised light (Fig. 4).

**Microanalysis:**

EPMA was carried out on the corroded metal and the edge of the hole (Figs. 5 & 6), the results show that the banded structure at the edge of the hole is similar to the banded corrosion on the surface of M91:137A. The black band (in Fig. 4) is rich in Fe, the green materials inside the hole are crystals (Fig. 7), which is bronze disease based on the ratio of Cu to Cl.

| Points | Description |
|---|---|
| **1** | Cuprite |
| **2** | Corroded eutectoid with Pb inclusion |
| **3, 4, 5** | α phase |
| **6, 7, 8** | The banded corrosion at the edge of the hole |
| **9** | Bronze disease inside the hole |
| **12, 13, 14** | The red corrosion products (in Fig. 4) next to the banded corrosion. |

| Point | Cu | Fe | Au | Ni | Sn | Pb | Zn | Ag | Hg | As | Sb | Bi | Co | S | Cl | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 83.68 | 0.03 | 0.00 | 0.00 | 0.12 | 0.04 | 0.00 | 0.10 | 0.08 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 84.05 |
| **2** | 27.02 | 1.26 | 0.01 | 0.04 | 43.85 | 13.04 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.24 | 0.03 | 0.07 | 1.40 | 86.95 |
| **3** | 64.48 | 1.64 | 0.08 | 0.02 | 7.24 | 0.00 | 0.00 | 0.02 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 73.48 |
| **4** | 89.15 | 2.18 | 0.00 | 0.01 | 3.79 | 0.00 | 0.00 | 0.02 | 0.05 | 0.00 | 0.00 | 0.04 | 0.02 | 0.00 | 0.00 | 95.25 |
| **5** | 71.87 | 0.25 | 0.00 | 0.00 | 6.97 | 0.65 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.11 | 0.00 | 0.37 | 0.16 | 80.40 |
| **6** | 36.94 | 1.60 | 0.00 | 0.00 | 0.02 | 0.25 | 0.03 | 0.15 | 0.00 | 0.00 | 0.01 | 0.07 | 0.00 | 0.01 | 0.38 | 39.46 |
| **7** | 8.01 | 46.31 | 0.00 | 0.02 | 0.00 | 3.22 | 0.00 | 0.02 | 0.00 | 0.00 | 0.00 | 0.00 | 0.08 | 0.45 | 0.23 | 58.33 |
| **8** | 76.52 | 8.61 | 0.14 | 0.00 | 0.00 | 0.09 | 0.00 | 0.07 | 0.09 | 0.11 | 0.00 | 0.00 | 0.00 | 0.03 | 0.57 | 86.25 |
| **9** | 52.63 | 0.48 | 0.00 | 0.00 | 0.00 | 0.41 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.02 | 18.74 | 72.29 |
| **12** | 64.66 | 0.39 | 0.08 | 0.00 | 0.00 | 0.34 | 0.00 | 0.03 | 0.00 | 0.09 | 0.05 | 0.00 | 0.01 | 0.00 | 0.24 | 65.88 |
| **13** | 75.73 | 0.11 | 0.09 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.03 | 0.38 | 0.00 | 0.05 | 0.00 | 0.05 | 1.44 | 77.87 |
| **14** | 49.72 | 1.16 | 0.00 | 0.00 | 4.35 | 2.14 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.08 | 0.87 | 58.33 |

EPMA spot analysis was also carried out on the dendrite Cu in the metal; the results are as follows (Figs. 8 & 9). BEI shows that some dendrite Cu has few pores (Fig. 8), while other dendrites of Cu have more pores (Fig. 9).

| point | Cu | Fe | Sn | Pb | S | Cl | Ag | Bi | As | Total |
|---|---|---|---|---|---|---|---|---|---|---|
| **15** | 92.01 | 0.03 | 0.03 | 0.04 | 0.01 | 0.00 | 0.08 | 0.00 | 0.00 | 92.21 |
| **16** | 91.48 | 0.05 | 0.20 | 0.00 | 0.02 | 0.00 | 0.06 | 0.01 | 0.00 | 91.82 |
| **17** | 93.75 | 0.03 | 0.05 | 0.04 | 0.02 | 0.00 | 0.05 | 0.00 | 0.00 | 93.93 |
| **18** | 93.35 | 0.02 | 0.04 | 0.06 | 0.02 | 0.00 | 0.06 | 0.04 | 0.00 | 93.58 |
| **19** | 80.41 | 0.05 | 0.26 | 0.01 | 0.02 | 0.15 | 0.07 | 0.19 | 1.38 | 82.52 |
| **20** | 81.08 | 0.47 | 5.43 | 1.32 | 0.10 | 0.22 | 0.10 | 0.32 | 6.58 | 95.62 |
| **21** | 93.58 | 0.05 | 0.19 | 0.02 | 0.00 | 0.03 | 0.03 | 0.02 | 0.00 | 93.92 |
| **22** | 90.46 | 0.05 | 0.03 | 0.00 | 0.02 | 0.00 | 0.11 | 0.04 | 0.00 | 90.71 |

## SUMMARY

It is a binary alloy of Cu-Sn with Fe. It has a dendritic structure. The bulk composition determined by SEM/EDS is 76% Cu and 16% Sn. The tin content seems to be over estimated due to the low total. Fe-rich corrosion and bronze disease are found in a hole in the metal. Redeposited Cu is present. It is likely that destannification has occurred in this sample.

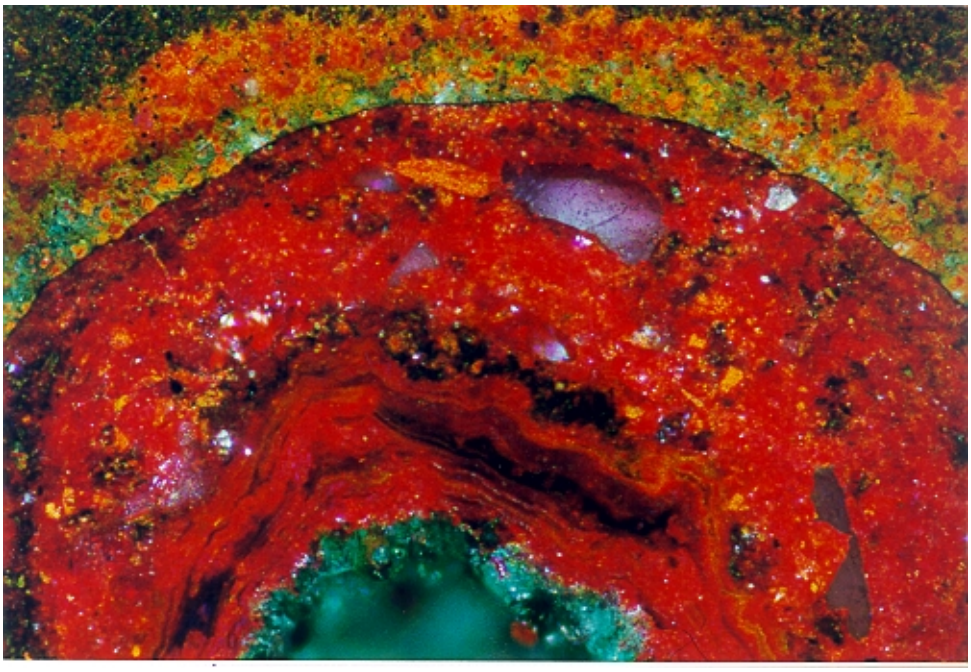


Fig. 4 Photomicrograph of the hole, showing the presence of Fe-enriched corrosion (black bands) and bronze disease (green one in the hole). C/P. Width of the image = 1 mm.

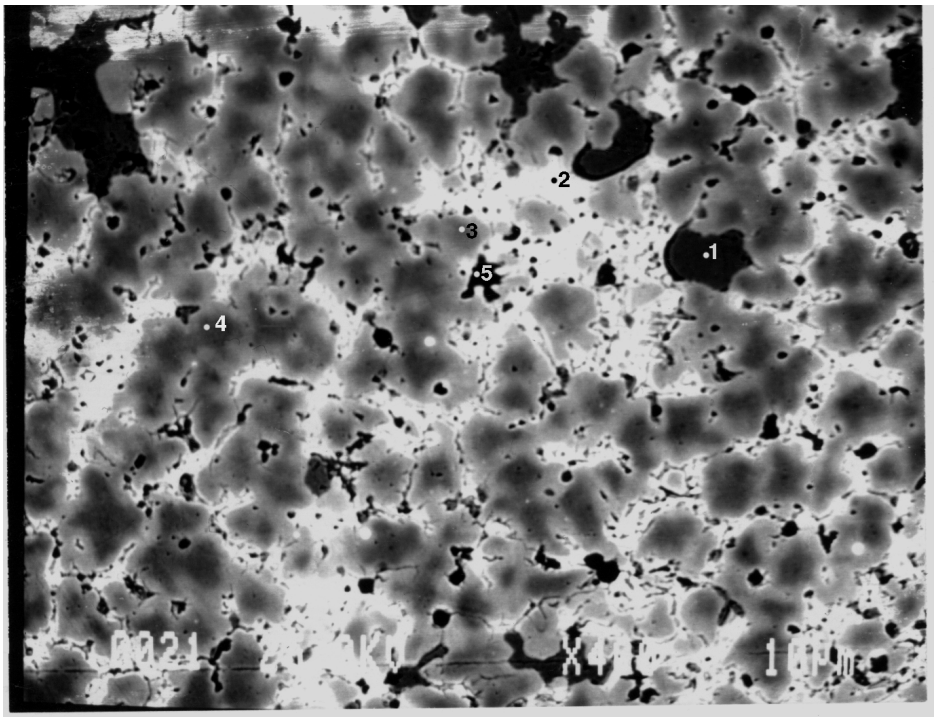



Fig. 5 BEI of corroded metal, showing EPMA points.

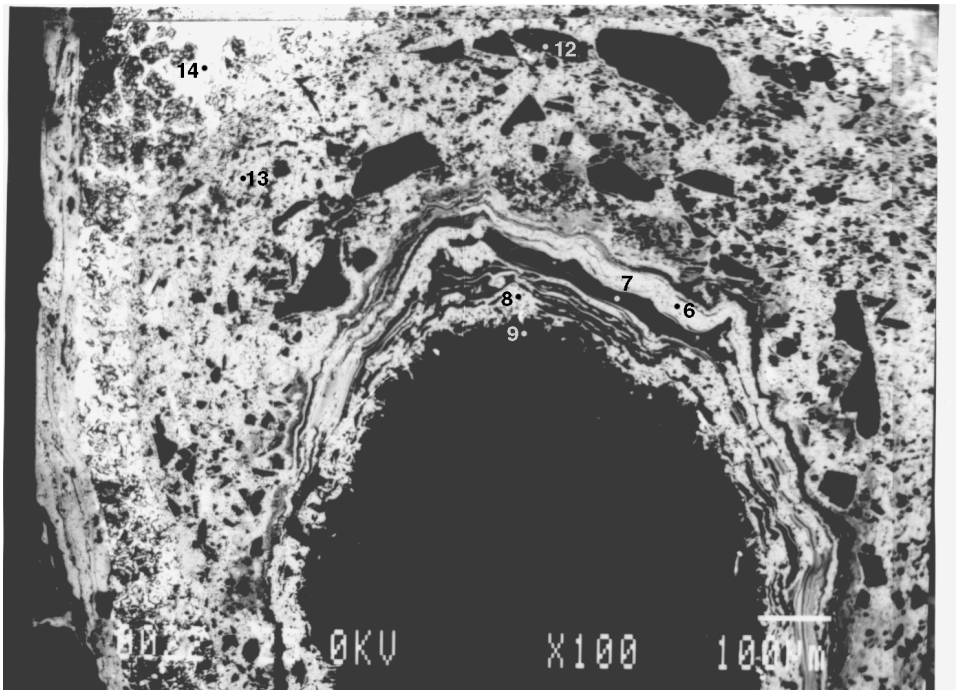



Fig. 6 BEI of the hole, showing EPMA points.


Fig. 7 BEI of crystals of bronze disease inside the hole.

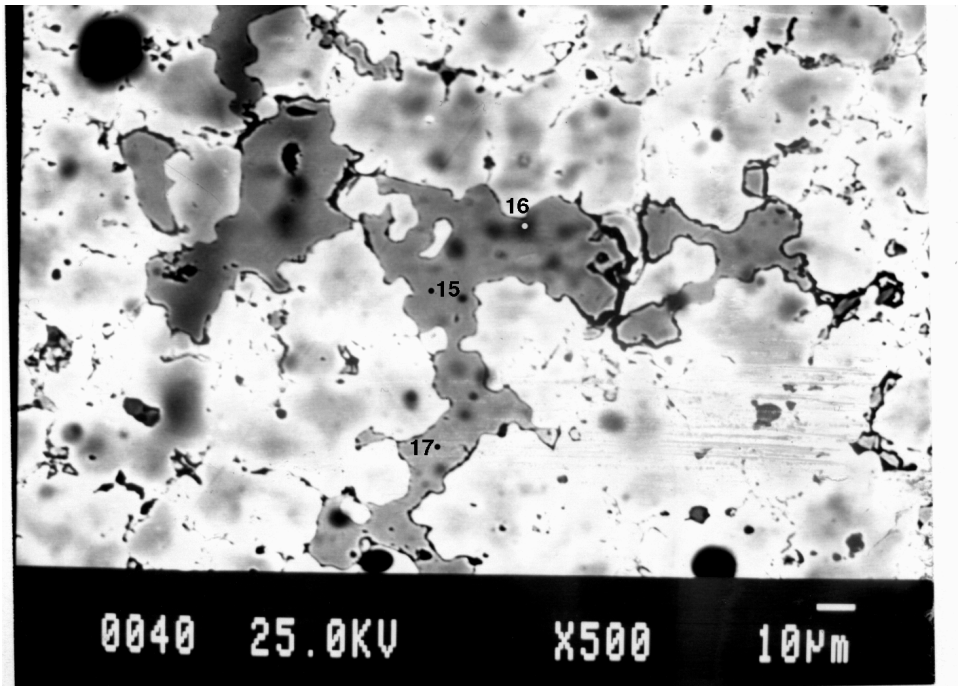



Fig. 8 BEI of Cu with few pores, showing EPMA points.

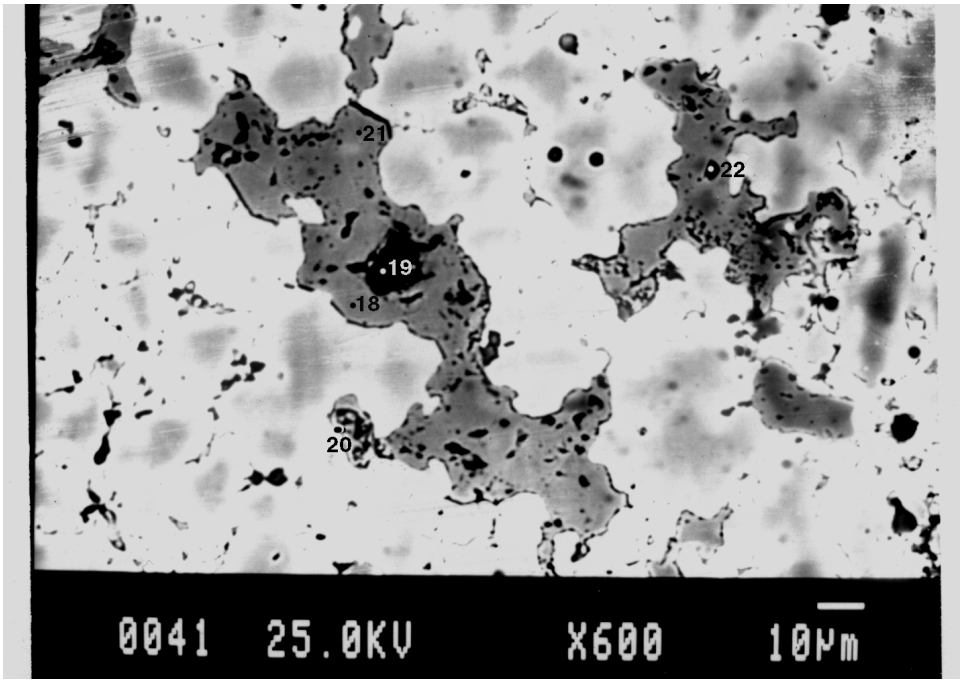



Fig. 9 BEI of Cu with more pores, showing EPMA points.

## GENERAL

**Object Number:** yoke 2

**Excavation Date:** 1998

**Origin:** No1 chariot pit at Xujiahutong, in east of Zhaochen site, Fufeng, Shaanxi

**Object:** horse fitting/yoke

**Date:** Middle or late Western Zhou

**Fragment Weight:** 2.5 g

**Fragment size:** 25x16x0.3 mm

**General description:**

This fragment is very thin. It has all sides broken. Corrosion index is 5. There is a corrosion overburden, including mainly green corrosion products and soil on the surface. No decoration is apparent (Fig. 1).

## TECHNICAL STUDIES OF METAL

**Metallographic structure:**

A section cut through the full width of the fragment was taken for metallographic observation. It is almost totally corroded, with only some isolated α phases being left (Fig. 2). The original surfaces are so badly disrupted that hardly to be seen. The estimated thickness is about 0.3 mm as measured in the metallographic section. Its structure can hardly be identified, it might be an equi-axed structure (Fig. 3).

**Composition:**

**AAS:** too corroded for analysis.

**Microanalysis:**

SEM/EDS semi-quantitative analysis was carried out on the corroded metal, the result shows that it is a binary alloy of Cu-Sn. Sn is over estimated due to corrosion.

| Cu | Sn | Total |
|---|---|---|
| 53.6 | 16.6 | 70.2 |

**Microhardness:** too corroded for measuring.

## CORROSION

**XRD results:** not carried out.

**Metallographic observation:**

Based on their characteristic colours in the metallographic section the corrosion layers are cuprite mixed with cassiterite, cuprite mixed with copper carbonate, and copper carbonate from the inner most surface outwards (Fig. 4).

**Microanalysis:**

EPMA was carried out on the corroded metal and corrosion overburden; the results are as follows:

| Points | Description |
|---|---|
| **1** | Remnant α phase |
| **2** | Corrosion inside the metal |
| **3** | Green corrosion in surface |
| **4** | Blue corrosion in surface |
| **5** | Red corrosion in surface |

| Point | Cu | Fe | Au | Ni | Sn | Pb | Zn | Ag | Hg | As | Sb | Bi | Co | S | Cl | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 74.26 | 0.02 | 0.00 | 0.01 | 15.46 | 0.16 | 0.00 | 0.05 | 0.00 | 0.00 | 0.00 | 0.04 | 0.00 | 0.02 | 0.05 | 90.06 |
| **2** | 40.83 | 0.04 | 0.07 | 0.00 | 28.39 | 1.09 | 0.00 | 0.00 | 0.04 | 0.06 | 0.00 | 0.03 | 0.00 | 0.00 | 0.17 | 70.72 |
| **3** | 39.04 | 0.03 | 0.02 | 0.00 | 29.99 | 1.22 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.10 | 0.00 | 0.02 | 0.03 | 70.45 |
| **4** | 51.87 | 0.03 | 0.00 | 0.00 | 0.34 | 0.00 | 0.00 | 0.10 | 0.08 | 0.00 | 0.00 | 0.09 | 0.00 | 0.04 | 0.07 | 52.63 |
| **5** | 69.90 | 0.00 | 0.01 | 0.00 | 0.02 | 0.00 | 0.00 | 0.03 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.17 | 70.14 |

## SUMMARY

It is a binary alloy of Cu-Sn with about 15% Sn in α phase. The original composition of bulk metal is not estimated, because it is severely corroded. It is likely an equi-axed structure. Bronze disease is absent, although it is almost totally corroded.

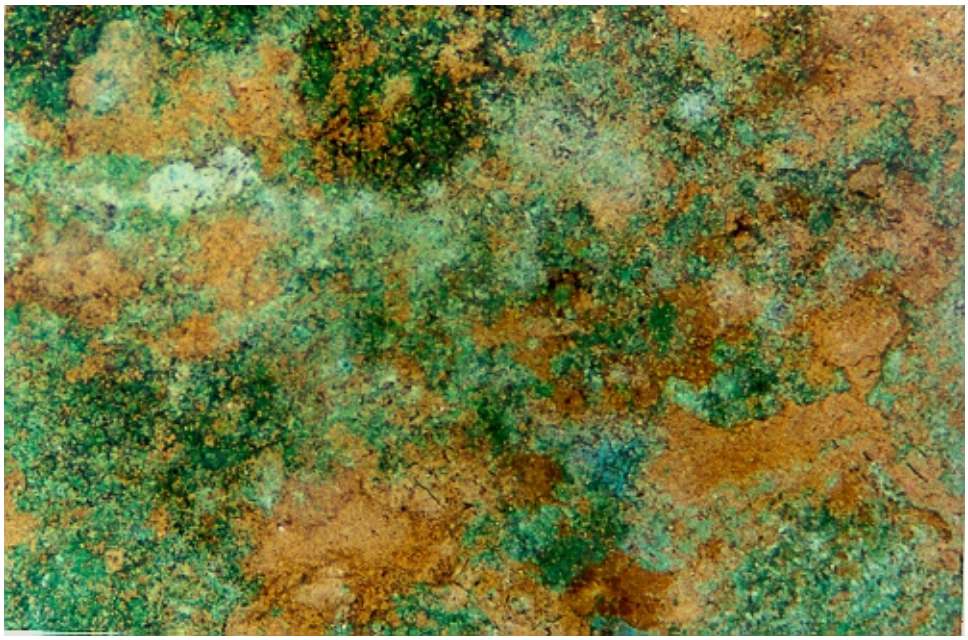


Fig. 1 General view of the fragment.
Width of the image = 7 mm.

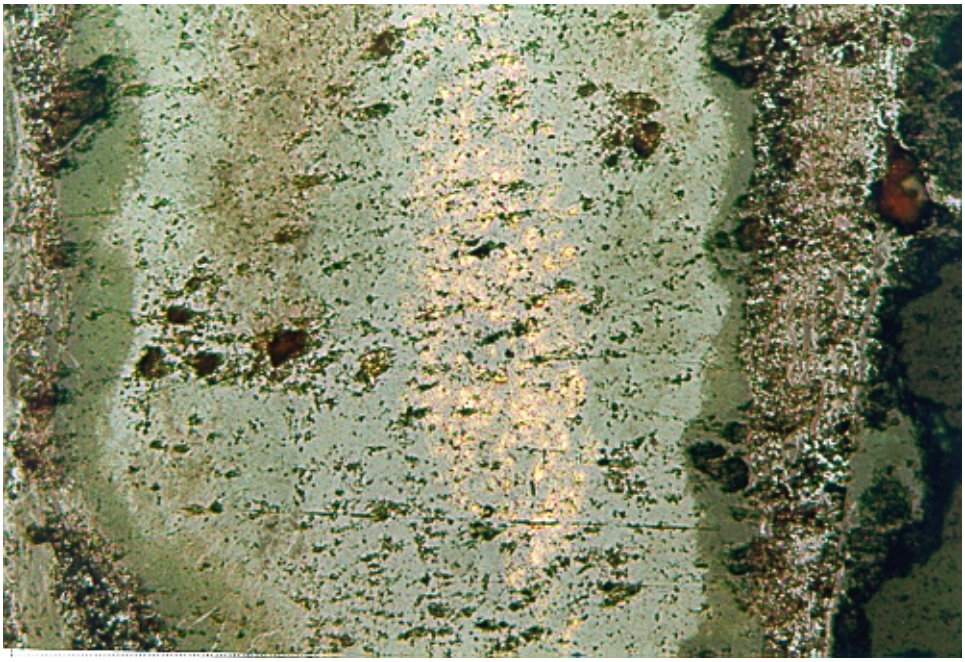


Fig. 2 Photomicrograph of corroded metal.
BF. Width of the image = 0.5 mm.

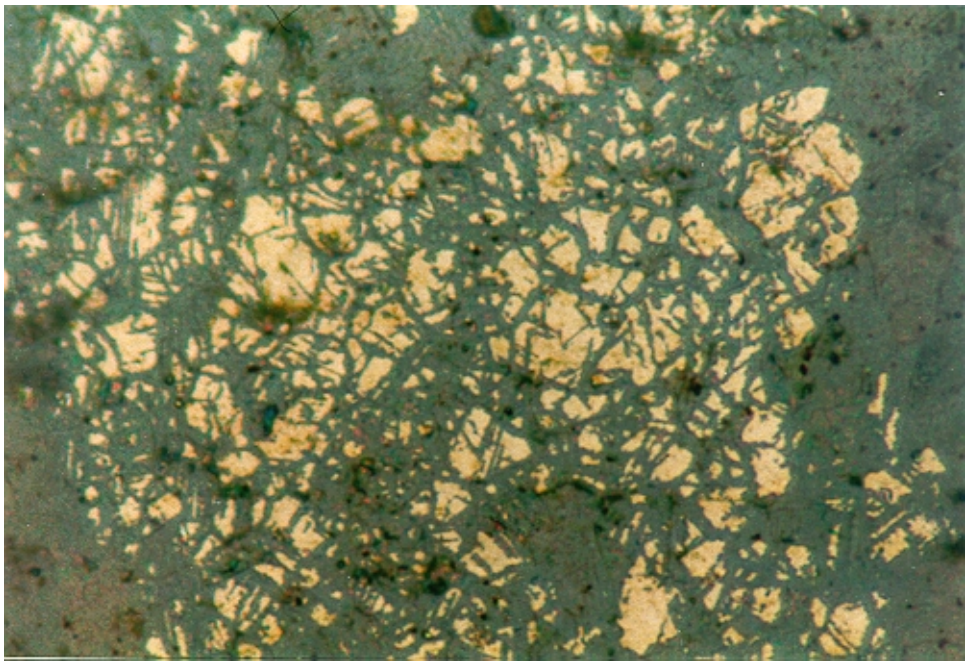


Fig. 3 Microstructure of corroded metal.

BF. Width of the image = 0.1 mm.

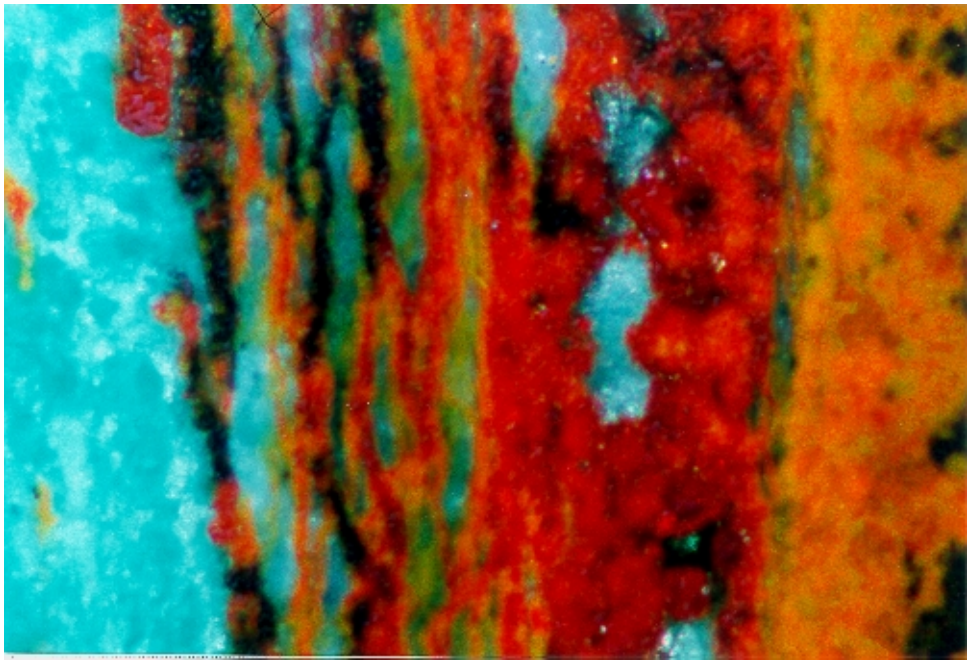


Fig. 4 Photomicrograph of layered corrosion overburden.

C/P. Width of the image = 0.5 mm.

## GENERAL

**Object Number:** yoke 3

**Excavation Date:** 1998

**Origin:** No1 chariot pit at Xujiahutong, in east of Zhaochen site, Fufeng, Shaanxi

**Object:** horse fitting /yoke

**Date:** Middle or late Western Zhou

**Fragment Weight:** 1.9 g

**Fragment size:** 22x14x(0.3-0.5) mm

**General description:**

This fragment looks like similar to yoke 2. Corrosion index is 5. The surface is covered with green and light green corrosion products and soil. Fibrous materials are also seen. Archaeologists thought it was probably from the same object as yoke 2.

## TECHNICAL STUDIES OF METAL

**Metallographic structure:**

A section cut through the full width of the fragment was taken for metallographic observation. This piece is very thin, with a thickness in the ranges of 0.3-0.5 mm as measured in the metallographic section (Fig. 1). It is totally corroded, and hardly to distinguish between the corroded metal and corrosion overburden. No metallic phase is seen at all. It looks very porous. A fibrous structure is seen in centre where used to be metal (Fig. 2).

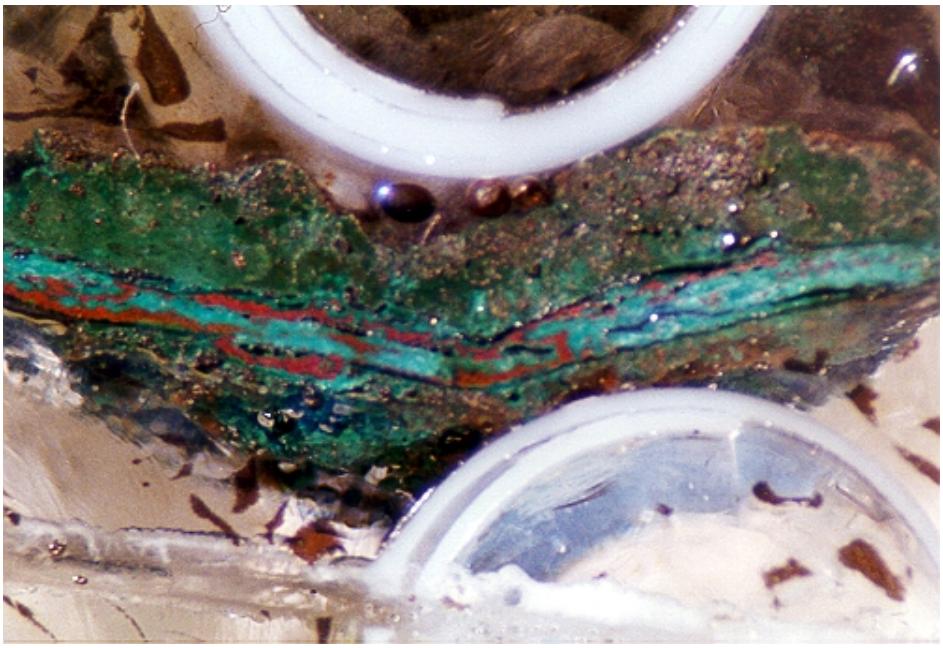


Fig. 1 Metallographic section. Width of the image = 7 mm.

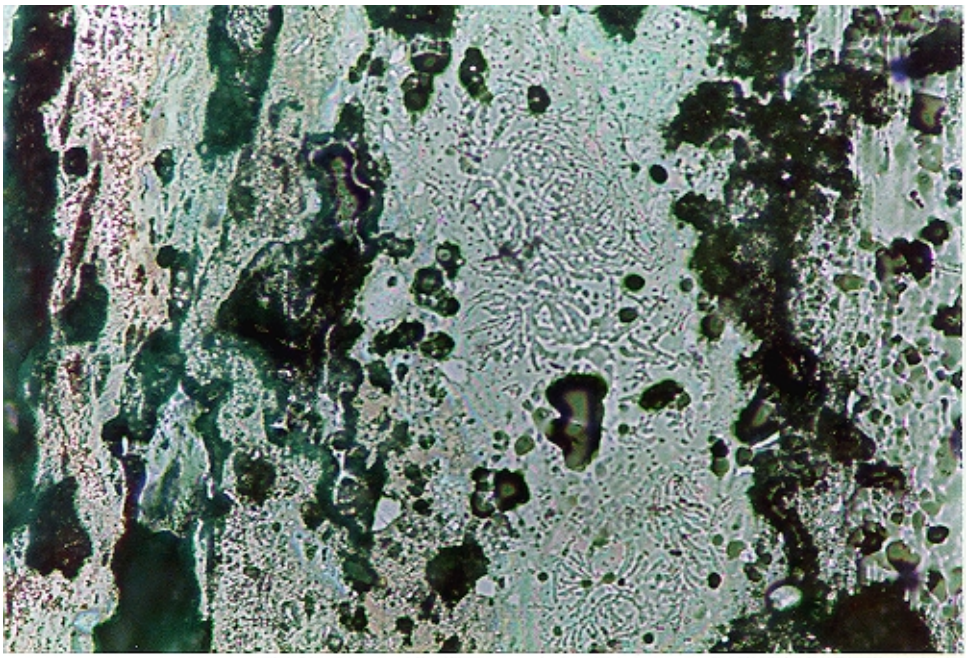


Fig. 2 Microstructure of corroded metal, showing fibrous structure.
BF. Width of the image = 1mm.

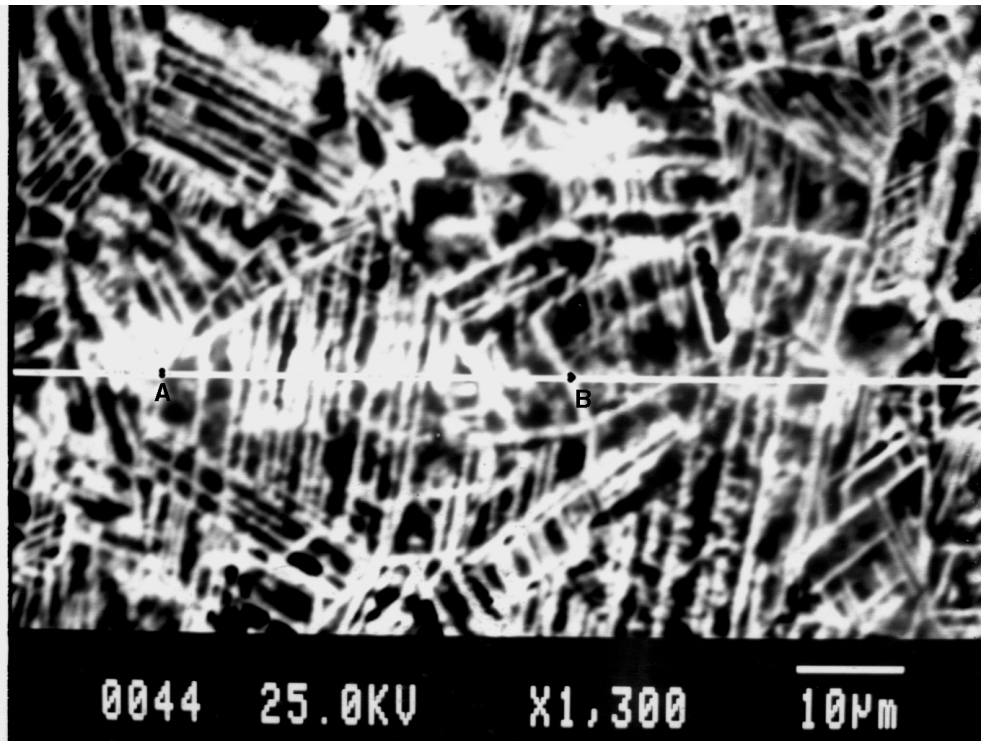



Fig. 3 BEI of corroded metal, showing 2-phases structure and EPMA linescan from A to B.

**Composition:**

**AAS:** too corroded for analysis.

**Microanalysis:**

See corrosion section

**Microhardness:** too corroded for measuring.

**CORROSION**

**XRD results:**

Surface sample: quartz, malachite, cuprite, copper sulphate hydrate.

**Metallographic observation:**

Corrosion overburden is thick on both sides of the original surfaces (Fig. 1). Similar to yoke 2, it is comprised of cuprite, copper carbonate and cassiterite based on their characteristic colours in the metallographic section.

**Microanalysis:**

Backscatterd electron image show that it is 2-phase structure (Fig. 3), which is same as that of M91:506A: principal grains and needle substructure inside the grains. In order to see if there is any difference in composition between the needles and the other part of the metal, EPMA linescan was carried out across a grain (Fig. 3 from A to B, interval: 1μm, 47 steps), the result is shown in Table1. The results show that it is a binary alloy of Cu-Sn. Fe and Pb is a little, with average concentrations being 0.08% and 0.72% respectively. Other elements such as As and Bi are almost absent. The ratio of Cu/Sn is different from that in M91:506A, although their structures are quite similar. A plot based on Table 1 is shown in Fig. 4. Unfortunately, Fig. 4 does not provide a clue about the original compositions and differences between two phases.

EPMA was carried out on the corroded metal (Fig. 5) and the corrosion overburden (Fig. 6); the results are shown in Table 2. It seems that bronze disease is present in this piece.

Table 1. The result of EPMA linescan from A to B

| No. | Cu | Fe | Sn | Pb | S | Cl | Ag | Bi | As | Total | Cu/Sn (atomic ratio) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 24.86 | 0.09 | 31.15 | 0.92 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 57.01 | 2.28 |
| **2** | 29.25 | 0.07 | 33.62 | 0.82 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 63.76 | 2.49 |
| **3** | 25.81 | 0.12 | 36.20 | 0.88 | 0.00 | 0.00 | 0.00 | 0.02 | 0.00 | 63.02 | 2.04 |
| **4** | 26.63 | 0.10 | 38.57 | 0.86 | 0.00 | 0.00 | 0.00 | 0.14 | 0.00 | 66.31 | 1.97 |
| **5** | 26.64 | 0.10 | 35.70 | 0.78 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 63.22 | 2.13 |
| **6** | 26.80 | 0.09 | 35.87 | 0.81 | 0.00 | 0.00 | 0.00 | 0.07 | 0.03 | 63.66 | 2.14 |
| **7** | 28.55 | 0.09 | 35.48 | 0.82 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 64.95 | 2.30 |
| **8** | 24.28 | 0.11 | 35.91 | 0.89 | 0.00 | 0.01 | 0.00 | 0.01 | 0.00 | 61.20 | 1.93 |
| **9** | 24.79 | 0.08 | 38.17 | 0.99 | 0.02 | 0.00 | 0.00 | 0.00 | 0.00 | 64.05 | 1.86 |
| **10** | 24.68 | 0.09 | 34.69 | 0.89 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 60.35 | 2.03 |
| **11** | 26.67 | 0.12 | 34.30 | 0.76 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 61.84 | 2.22 |
| **12** | 34.83 | 0.04 | 23.67 | 0.58 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 59.12 | 4.21 |
| **13** | 26.64 | 0.10 | 32.05 | 0.72 | 0.02 | 0.01 | 0.00 | 0.10 | 2.67 | 62.31 | 2.38 |
| **14** | 27.47 | 0.11 | 34.23 | 0.83 | 0.03 | 0.00 | 0.00 | 0.15 | 1.92 | 64.74 | 2.29 |
| **15** | 35.02 | 0.08 | 24.00 | 0.67 | 0.01 | 0.00 | 0.05 | 0.09 | 0.00 | 59.92 | 4.17 |
| **16** | 40.06 | 0.06 | 23.33 | 0.73 | 0.02 | 0.00 | 0.00 | 0.08 | 0.00 | 64.27 | 4.91 |
| **17** | 31.02 | 0.04 | 29.31 | 0.55 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 60.91 | 3.03 |
| **18** | 32.38 | 0.06 | 30.70 | 0.62 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 63.76 | 3.02 |
| **19** | 29.35 | 0.08 | 33.81 | 0.78 | 0.00 | 0.00 | 0.01 | 0.10 | 0.00 | 64.13 | 2.48 |
| **20** | 29.56 | 0.09 | 30.88 | 0.76 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 61.30 | 2.74 |
| **21** | 29.88 | 0.08 | 32.80 | 0.67 | 0.00 | 0.00 | 0.00 | 0.07 | 0.00 | 63.50 | 2.60 |
| **22** | 21.77 | 0.08 | 36.13 | 0.77 | 0.01 | 0.00 | 0.00 | 0.07 | 0.00 | 58.83 | 1.72 |
| **23** | 20.29 | 0.09 | 40.65 | 0.89 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 61.92 | 1.43 |
| **24** | 25.15 | 0.09 | 34.36 | 0.83 | 0.03 | 0.00 | 0.00 | 0.00 | 0.00 | 60.46 | 2.09 |
| **25** | 34.25 | 0.07 | 23.97 | 0.61 | 0.02 | 0.00 | 0.00 | 0.00 | 0.00 | 58.91 | 4.09 |
| **26** | 37.94 | 0.06 | 25.58 | 0.59 | 0.00 | 0.00 | 0.00 | 0.04 | 0.00 | 64.21 | 4.24 |
| **27** | 34.69 | 0.07 | 24.17 | 0.60 | 0.00 | 0.00 | 0.02 | 0.06 | 0.00 | 59.60 | 4.10 |
| **28** | 35.77 | 0.05 | 25.64 | 0.60 | 0.03 | 0.00 | 0.01 | 0.00 | 0.00 | 62.10 | 3.99 |
| **29** | 32.36 | 0.08 | 23.97 | 0.59 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 57.00 | 3.86 |
| **30** | 37.38 | 0.08 | 22.14 | 0.69 | 0.02 | 0.00 | 0.00 | 0.05 | 0.00 | 60.35 | 4.83 |
| **31** | 39.74 | 0.04 | 23.65 | 0.59 | 0.00 | 0.00 | 0.00 | 0.12 | 0.00 | 64.16 | 4.80 |
| **32** | 28.14 | 0.07 | 32.70 | 0.64 | 0.03 | 0.01 | 0.00 | 0.07 | 0.00 | 61.66 | 2.46 |
| **33** | 25.08 | 0.10 | 36.24 | 0.81 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 62.23 | 1.98 |
| **34** | 31.11 | 0.04 | 26.67 | 0.55 | 0.00 | 0.00 | 0.05 | 0.12 | 0.00 | 58.54 | 3.34 |
| **35** | 33.24 | 0.06 | 29.24 | 0.80 | 0.00 | 0.00 | 0.08 | 0.00 | 0.00 | 63.42 | 3.25 |
| **36** | 34.60 | 0.10 | 30.92 | 0.75 | 0.03 | 0.00 | 0.03 | 0.11 | 0.00 | 66.53 | 3.20 |
| **37** | 26.40 | 0.09 | 32.38 | 0.76 | 0.01 | 0.00 | 0.08 | 0.08 | 0.00 | 59.81 | 2.33 |
| **38** | 30.14 | 0.08 | 31.41 | 0.69 | 0.01 | 0.00 | 0.06 | 0.05 | 0.00 | 62.44 | 2.74 |
| **39** | 29.72 | 0.08 | 28.56 | 0.61 | 0.01 | 0.01 | 0.04 | 0.05 | 0.00 | 59.08 | 2.98 |
| **40** | 29.96 | 0.09 | 32.02 | 0.73 | 0.02 | 0.00 | 0.00 | 0.00 | 0.00 | 62.82 | 2.68 |
| **41** | 35.53 | 0.01 | 24.42 | 0.55 | 0.00 | 0.00 | 0.04 | 0.00 | 0.00 | 60.55 | 4.16 |
| **42** | 29.25 | 0.10 | 31.69 | 0.73 | 0.02 | 0.01 | 0.05 | 0.05 | 0.00 | 61.89 | 2.64 |
| **43** | 26.65 | 0.08 | 34.85 | 0.66 | 0.02 | 0.01 | 0.00 | 0.03 | 0.00 | 62.30 | 2.19 |
| **44** | 29.74 | 0.06 | 27.49 | 0.56 | 0.01 | 0.00 | 0.04 | 0.06 | 0.00 | 57.96 | 3.09 |
| **45** | 32.29 | 0.06 | 28.16 | 0.75 | 0.00 | 0.00 | 0.00 | 0.16 | 0.20 | 61.61 | 3.28 |
| **46** | 31.74 | 0.06 | 26.39 | 0.50 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 58.68 | 3.44 |
| **47** | 33.88 | 0.06 | 27.32 | 0.67 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 61.94 | 3.55 |

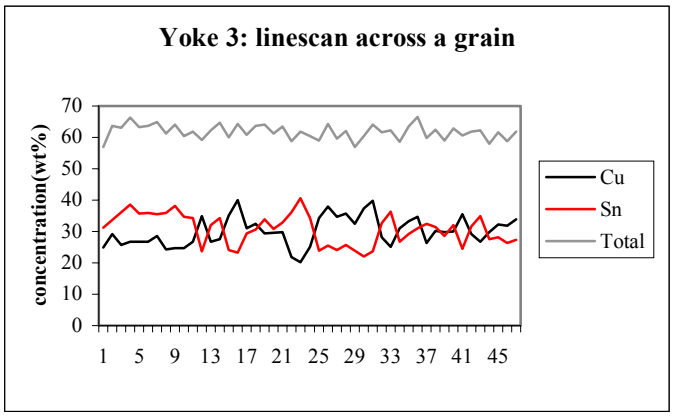



Fig. 4 EPMA linescan from A to B (Shown in Fig. 3)

Table 2 Results of EPMA point analysis

| points | Description |
|---|---|
| **1 – 5** | Corroded metal |
| **6 - 9** | Corrosion overburden |

| point | Cu | Fe | Au | Ni | Sn | Pb | Zn | Ag | Hg | As | Sb | Bi | Co | S | Cl | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 50.82 | 0.05 | 0.00 | 0.00 | 24.09 | 0.29 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.27 | 1.49 | 77.00 |
| **2** | 38.06 | 0.20 | 0.08 | 0.00 | 28.97 | 0.78 | 0.00 | 0.08 | 0.09 | 0.00 | 0.00 | 0.11 | 0.00 | 0.20 | 6.90 | 75.47 |
| **3** | 26.90 | 0.07 | 0.02 | 0.00 | 29.24 | 0.78 | 0.00 | 0.00 | 0.05 | 0.06 | 0.00 | 0.00 | 0.00 | 0.10 | 0.01 | 57.23 |
| **4** | 45.85 | 0.03 | 0.08 | 0.00 | 26.65 | 0.80 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.40 | 0.74 | 74.55 |
| **5** | 33.04 | 0.07 | 0.02 | 0.00 | 31.57 | 0.95 | 0.00 | 0.00 | 0.00 | 0.03 | 0.00 | 0.19 | 0.00 | 0.04 | 0.21 | 66.12 |
| **6** | 49.59 | 0.01 | 0.00 | 0.00 | 0.73 | 0.18 | 0.00 | 0.02 | 0.00 | 0.00 | 0.00 | 0.04 | 0.00 | 0.05 | 9.19 | 59.81 |
| **7** | 50.40 | 0.01 | 0.00 | 0.00 | 0.07 | 0.22 | 0.00 | 0.01 | 0.04 | 0.04 | 0.00 | 0.00 | 0.00 | 0.03 | 0.00 | 50.82 |
| **8** | 37.30 | 0.07 | 0.00 | 0.01 | 25.21 | 0.57 | 0.00 | 0.00 | 0.04 | 0.21 | 0.00 | 0.19 | 0.00 | 0.05 | 0.00 | 63.63 |
| **9** | 49.45 | 0.00 | 0.01 | 0.00 | 0.06 | 0.00 | 0.00 | 0.05 | 0.13 | 0.00 | 0.00 | 0.00 | 0.00 | 0.06 | 0.00 | 49.75 |

## SUMMARY

It is a binary alloy of Cu-Sn with 2-phase structure: needles within grains. It could be the result of working or bending. This will be discussed in Chapter 5. The original composition is not estimated, because it is totally corroded. This fragment was not from the same object as yoke 2 based on its microstructure.

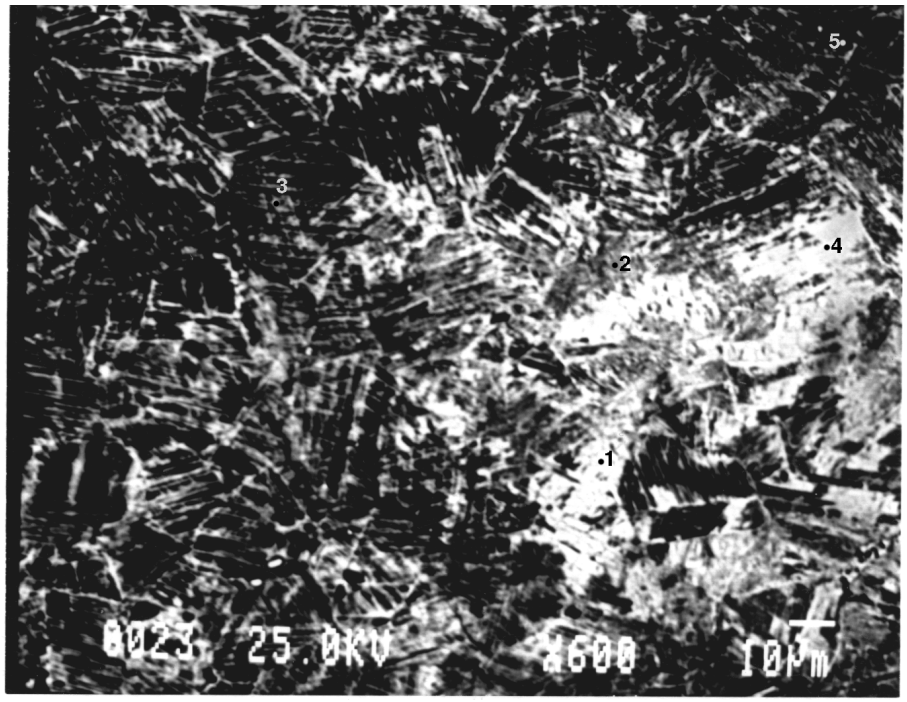



Fig. 5 BEI of corroded metal, showing EPMA points.

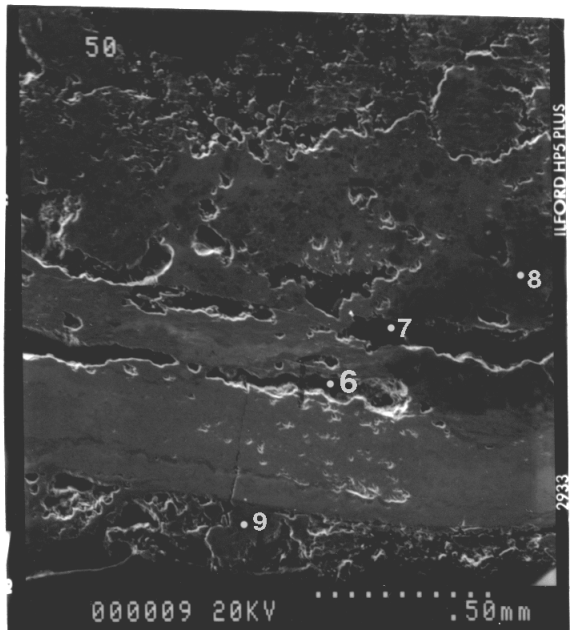



Fig. 6 SEI of metallographic section, showing EPMA points.