Southern African Field Archaeology 6:26-37. 1997.

ARCHAEOMETALLURGICAL STUDIES IN MARITIME ARCHAEOLOGY AT THE CAPE OF GOOD HOPE*

DUNCAN MILLER

Department of Archaeology,
University of Cape Town,
Rondebosch 7701

*Accepted for publication July 1997

ABSTRACT

Few metal artefacts recovered from maritime archaeological contexts in southern Africa have been subject to metallographic or chemical analysis. This paper presents several case studies to illustrate some of the questions that can be addressed with the analysis of maritime metals and corrosion products.

INTRODUCTION

This paper summarises a series of studies conducted in the Archaeology Materials Laboratory, University of Cape Town, aimed at solving specific problems in the interpretation of metal artefacts recovered from maritime sites near Cape Town.

The first set of samples was from a pair of large bronze cannon recovered on 11 February 1989 by Bruno Werz (University of Cape Town) from the wreck of the Dutch East Indiaman "Oosterland" which foundered in Table Bay on 24 May 1697 (Werz 1992:85,87). These cannon are now housed in the Maritime Museum, Waterfront, Cape Town. These were sampled for compositional analysis to determine the nature of the bronze alloy used in their manufacture. A fragment of corrosion product from the inside of the breech of a bronze swivel gun recovered from the "Oosterland" was also analyzed for comparison. Drill turnings or swarf from an unidentified bronze cannon in the Cape Town Castle were made available by David Halkett (University of Cape Town) for comparison.

The second set of samples consisted of several sheets of copper and what appeared to be corroded examples of similar copper sheeting also recovered from the "Oosterland" by Bruno Werz. These were investigated to attempt to confirm the identification of the corroded material. There were morphological similarities in the shape of the copper sheets and the corroded objects. There were examples of flat copper sheeting, with irregular edges as well as right angle corners. In some instances there were copper rivets and nails still attached to this sheeting. There were also elongated strips of metal, generally about 50 - 100 mm wide, with a sharp fold along one long edge, and a row of more or less equally spaced nail holes along the other. These features were reflected in the corroded specimens, but were largely obscured by the corrosion product. There were sheared sheets, and elongated strips with a curve along one side, and in a few cases indentations that may have represented nail holes like those present in the copper sheet.

The third set of samples studied consisted of three copper bars recovered by Bruno Werz from another Dutch wreck near Cape Town, identified by him as the "Waddinxsveen" (dating to 1697). One of the copper bars was sampled and analyzed metallographically prior to sending it to the British Museum for trace element analysis in an attempt to identify the origin of the copper.

The fourth set of samples consisted of four bronze samples recovered by Jaco Boshoff of the Maritime Museum, Cape Town. These were analyzed to determine the degree of similarity between them, and to try to identify the provenance of one of them which came from a disassociated rudder.

ANALYTICAL METHODS

In the case of the "Oosterland" cannon a single 5 g fragment was removed from one of the eroded handles by careful, water-cooled sawing with a fine hacksaw. This sample was removed under National Monuments Council Permit No. 8/94/02/003/30. Several fragments of corrosion product had been retained from the inside of the barrel of the other cannon prior to cleaning and restoration, and a piece of this was analyzed so as not to damage the intact metal. In the other cases, except for the bronze turnings, small sections were removed with a water-cooled rotary diamond saw. Each sample, including the bronze swarf, was mounted separately in acrylic resin under vacuum to remove air bubbles, and ground and polished on rotary laps, with a final ¼ micron diamond polish.

The polished and subsequently etched sections were

studied with a Reichert-Jung Polyvar dual metallographic/ petrographic microscope, using plane polarised light and Nomarski differential interference contrast where appropriate (Snyman 1989). Grain size was established by visual comparison with standard charts (ASTM 1981). Microhardness was determined with a Shimadzu microhardness tester fitted with a Vickers microhardness indenter, except for some samples tested later with a Knoop indenter because the Vickers indenter on the available instrument was damaged. Knoop microhardness is sensitive to anisotropy, both crystallographic and microstructural, so determinations were made in various orientations on each specimen in order to minimise this effect. Knoop microhardness is not standard for archaeometallurgical purposes but values can be compared approximately with Vickers microhardness values by dividing by 1,087 (Ross 1985:5). The adjusted values are given in square brackets after the measured Knoop microhardness values.

The chemical analyses were carried out in the Electron Microscope Unit, UCT, using the Cambridge S200 and S400 scanning electron microscopes (SEM) with energy dispersive X-ray fluorescence micro-analysis systems (EDS). Analyses were done in raster mode for the determination of bulk compositions and in spot mode, with an analytical volume of about 1 micron diameter, for the determination of composition in selected locations. Software ZAF corrections were applied to the analytical results to produce semi-quantitative elemental analyses expressed as percentages normalised to 100 percent. This system has a precision of about 1 percent for the detectable elements, in this case those with atomic weights heavier than sodium. The lower limit of detection is about 0,1 percent under optimal conditions. This means that values below 1 percent only represent presence or absence information.

DESCRIPTIONS AND ANALYTICAL RESULTS

"Oosterland" bronze cannon specimen

The irregularly shaped 5 g bronze sample measured 16 mm by 7 mm by 6 mm and its removal left a neat, flat surface at the base of the eroded cannon handle selected for sampling and analysis (Figs 1 & 2). Under the reflected light microscope, the polished sample exhibited severe casting porosity and had a large crack partly filled with grey corrosion products (Fig. 3). The metal was a bronze containing approximately 3,4 % tin dissolved in copper (Table 1:Oost3a-c). Etching for 10 seconds in an $FeCl_3$ solution revealed the coarse grain size, greater than ASTM 0, due to very slow cooling of the bulky casting. The metal was single phase, as is to be expected from a low tin bronze (Scott 1991).

There were numerous dual component inclusions which were rounded or globular, predominantly light blue-grey in reflected plane polarised light, with some irregular darker patches (Fig. 4). There were a few less numerous granular-looking inclusions which were not identifiable optically. The inclusions bore no relation to the existing grain boundaries which indicated that they had not been soluble in the molten metal. The EDS analysis of selected inclusions (Table 1:Oost3d-f) indicated that the inclusions consisted mostly of lead, commonly added to low tin bronzes to facilitate casting (Scott 1991:27).

Fig. 1 Photograph of the eroded bronze cannon handle from the "Oosterland" from which the sample was removed (scale in cm).

Fig. 2 Photograph of the bronze cannon from the "Oosterland" showing the sampled area and the sample removed.

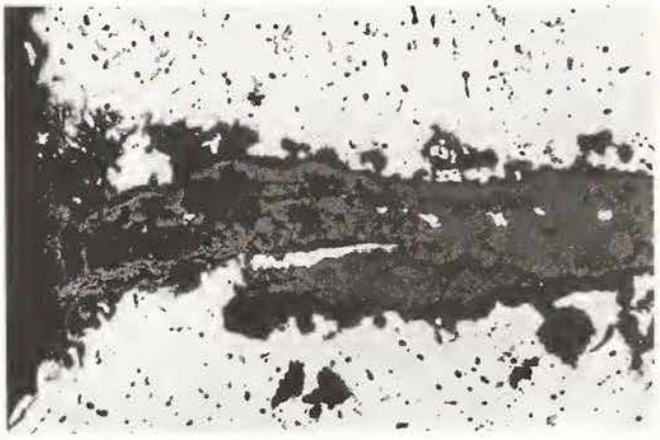

Fig. 3 Micrograph of the polished sample from the "Oosterland" cannon showing a corrosion filled crack and the casting porosity (dark voids) (15 X).

Fig. 4 Micrograph showing the lead-rich light blue-grey inclusions in the "Oosterland" cannon (112 X).

Fig. 5 Photograph of sample of corrosion layer from the inside of a bronze cannon recovered from the "Oosterland" (scale in mm).

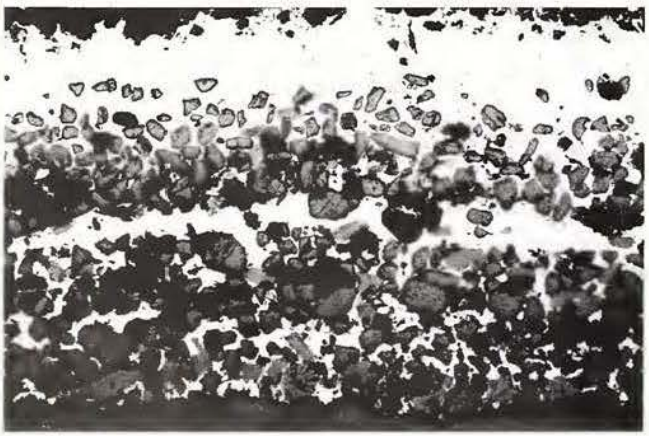

Fig. 6 Polished section of corrosion layer from the inside of a bronze cannon recovered from the "Oosterland" showing layered structure (15 X).

Corrosion rind from bronze cannon

This sample was a fragment of the corrosion product from inside the second cannon, known to have been cast in 1685 (Werz 1989:16; Werz 1992:86).

The sample was a slightly curved, blueish-black sheet,

Fig. 7 Polished section of corrosion product from the inside of a bronze cannon recovered from the "Oosterland" showing finely banded layer devoid of sand grains (112 X).

with visible layering and bright green patches of copper corrosion product on both sides (Fig. 5). The convex-surface, presumably the one closest to the original metal, was slightly lighter in colour. The sample was 81,4 mm long, 42,8 mm wide, and varied from 2,2 mm to 3,8 mm in thickness. It had a mass of 17,69 g, and was non-magnetic.

In transverse section the material was clearly layered (Fig. 6). There were five layers. The outermost layer, originally nearest the metal, was thin, very porous, and consisted of structureless masses of cuprite (Cu_2O) and malachite ($CuCO_3$) containing sparse tiny rounded metallic droplets. The second layer, the broad light one in Fig. 6, consisted of finely banded blueish-white corrosion product, with no included sand grains, and what appeared to be the distorted ghost remnants of the former crystalline structure (Fig. 7). A raster bulk analysis of this layer indicated a composition of copper sulphide with 2,8% tin content, clearly derived from the parent bronze (Table 1:Oost4 a). The next layer was crowded with sand grains which became more dense towards the upper surface. This was followed by a second layer of relatively sand free light blue corrosion product and a final sandy layer, itself possibly internally banded.

The main corrosion product appeared to be mostly very fine grained cuprite and malachite. The microscopic banding in the second layer (Fig. 7) probably represented the corrosion of the original metal surface. The metallic droplets were probably reprecipitated copper resulting from the dissolution of the parent bronze (*cf.* Scott 1991:fig. 71).

Corrosion rind from breech of bronze swivel gun

This was a fragment of lamellar corrosion product removed from the interior of the breech of a bronze swivel gun recovered from the "Oosterland" by Bruno Werz. The sample was a slightly curved, blue-black sheet, similar in appearance to the cannon corrosion sample. There was a red copper oxide layer on the surface originally in contact with the metal, and corroded

Table 1. Results of energy dispersive X-ray fluorescence analysis.

SAMPLE (mode)	ELEMENTS WT. %										
	Si	S	Fe	Ni	Cu	As	Sr	Ag	Sn	Sb	Pb
Oost1 a inclusion (s)	-	-	-	-	15,5	7,6	3,5	-	-	21,0	52,4
Oost1 b inclusion (s)	-	-	-	-	45,0	6,8	1,8	-	-	5,9	40,6
Oost1 c crystals (r)		9,2	0,6	1,9	59,8	4,1	0,5	-	-	2,9	21,5
Oost1 d crystals (s)	-	10,0	0,4	0,7	56,1	7,3	-	-	-	2,6	22,9
Oost2 a rivet (r)	-	-	-	-	100	-	-	-	-	-	-
Oost2 b plate (r)	-	-	-	-	100	-	-	-	-	-	-
Oost2 c cuprite (s)	-	-	-	-	100	-	-	-	-	-	-
Oost2 d glass (r)	-	-	-	-	24,3	9,1	-	-	-	2,9	63,7
Oost2 e glass (r)	-	-	-	-	26,1	5,3	3,1	-	-	6,1	59,6
Oost2 f glass (r)	-	-	-	-	21,0	7,1	3,8	-	-	3,3	65,7
Oost2 g glass (s)	-	-	-	-	36,4	3,5	2,7	-	-	6,5	49,8
Oost2 h glass (s)	-	-	-	-	14,7	29,5	2,7	-	-	9,9	43,2
Oost3 a bulk (r)	-	0,3	-	-	96,5	-	-	-	3,6	-	-
Oost3 b bulk (r)	-	0,2	-	-	96,9	-	-	-	3,2	-	-
Oost3 c bulk (r)	-	0,3	-	-	96,6	-	-	-	3,4	-	-
Oost3 d inclusion (s)	-	-	-	-	7,3	-	4,7	-	-	-	88,0
Oost3 e inclusion (s)	-	6,1	-	-	4,2	-	1,1	0,7	-	-	87,6
Oost3 f inclusion (s)	-	-	-	-	6,6	-	4,4	-	-	-	89,0
Oost4 a corrosion (r)	3,4	10,2	-	-	83,6	-	-	-	2,8	-	-
Oost5 a corrosion (r)	0,8	9,1	3,9	-	79,2	2,5	-	-	4,6	-	-
Oost5 b corrosion (r)	3,9	10,4	2,8	-	81,0 (+Zn 1,6)		-	-	0,3	-	-
Oost5 c corrosion (r)	-	10,8	-	-	89,2	-	-	-	-	-	-
Swarf a metal (r)	-	-	-	-	96,0	-	-	-	4,0	-	-
Ssarf b inclusion (r)	-	12,1	-	-	87,9	-	-	-	-	-	-
Swarf c metal (s)	-	-	-	-	93,6	2,7	-	-	3,7	-	-
Bar a bulk (r)	0,4	0,7	-	-	98,9	-	-	-	-	-	-
Bar b bulk (r)	0,2	0,4	-	-	99,4	-	-	-	-	-	-
Bar c inclusion (s)	-	0,9	-	-	98,5	0,7	-	-	-	-	-
Bar d inclusion (s)	-	0,6	0,2	-	97,9	1,3	-	-	-	-	-
Bar e inclusion (s)	-	0,4		-	99,3	-	-	-	-	-	-
Bar f inclusion (s)	-	0,4		-	99,6	-	-	-	-	-	-
JB1 a bulk (r)	-	-	-	-	97,0	-	-	-	2,9	-	0,2
JB1 b inclusion (s)	-	22,0	-	-	78,0	-	-	-	-	-	-
JB2 a bulk (r)	-	-	-	-	93,7	-	-	-	5,6	-	0,7
JB2 b inclusion (r)	-	23,8	3,3	-	72,9	-	-	-	-	-	-
JB2 c inclusion (r)	-	-	-	-	77,1	-	-	-	22,9	-	-
JB2 d inclusion (r)	-	-	-	-	95,1	-	-	-	5,0	-	-
JB3 a bulk (r)	-	-	-	-	94,6	-	-	-	4,3	-	1,0
JB4 a bulk (r)	-	-	-	-	94,5	-	-	-	5,0	-	0,5

pepper corns trapped in the corrosion product adhering to the exposed surface. The sample was 8,87 g in mass, with a length of 50 mm, a breadth of 30 mm and an average thickness estimated to be about 4 mm.

A polished transverse section revealed a layered structure (Fig. 8).

i. The innermost layer was finely laminated, with some voids. It consisted of acicular blue inclusions which were probably remnants of an original metal

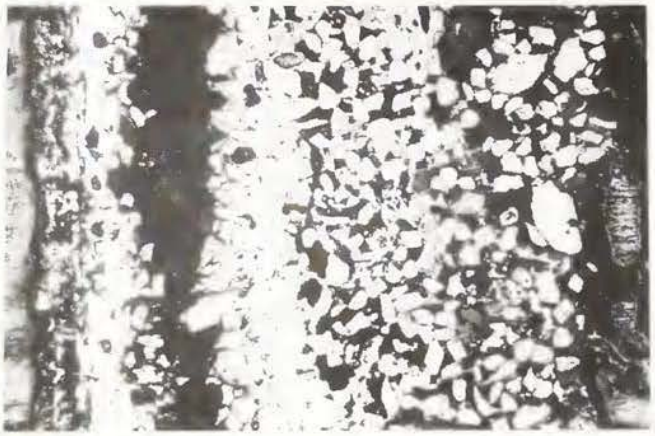

Fig. 8. Polished section of corrosion product from the inside of the breech of a bronze swivel gun recovered from the "Oosterland" showing layered structure (15 X).

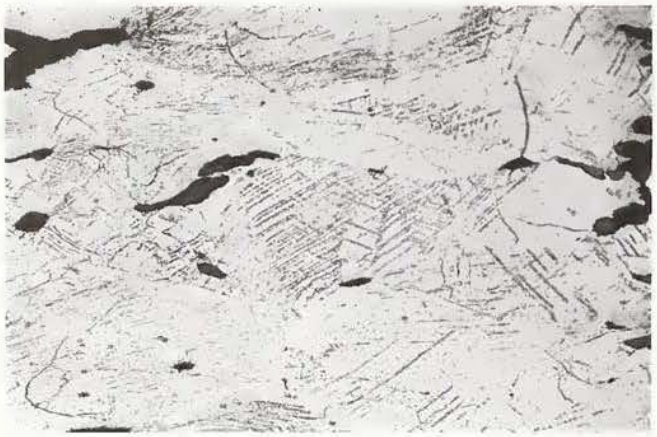

Fig. 9 Etched section of bronze cannon swarf showing slip bands due to intense strain (180 X).

phase set in a blue oxide with no red reflections. This was not cuprite and optically it had the appearance of covellite, with very strong bireflectance and characteristic anisotropy (Craig & Vaughan 1981:336). Two bulk analyses of this layer showed it to contain about 10% sulphur and 80% copper overall, with the balance consisting of variable amounts of silica, iron, arsenic, zinc and tin (Table 1:Oost5 a & b).

ii. The middle layer consisted of quartz and calcite grains set in a light blue massive matrix which appeared isotropic under crossed polarised light. This layer was not analyzed.

iii. The outer layer consisted of a blue matrix with a composition of about 11% sulphur with a balance of 89% percent copper (Table 1:Oost5 c), containing numerous voids and included quartz grains with bright crystalline overgrowth which were probably calcite.

These analyses were very similar to those from the "Oosterland" bronze cannon and it is likely that they all had very similar if not identical bronze compositions.

Fig. 10 Polished transverse section of corroded sheet from the "Oosterland" showing the layered structure (7,2 X).

Bronze cannon swarf

This sample, submitted by Mr David Halkett, consisted of drill turnings from an unidentified bronze cannon housed at the Cape Town Castle.

The severe deformation of the turnings made a microstructural analysis impossible. In polished section etched with $NH_4OH:H_2O_2$ the grains displayed numerous twins and slip bands due to severe strain (Fig. 9). The metal was an even yellow with scattered blue inclusions showing a faint unevenness in colour. The highly strained metal grains had an elevated Vickers microhardness of HV 242 (200 g, 10 s, n = 2, 228 & 256). The raster bulk analysis of an approximately 40 micron square area indicated that the metal was a 4% tin bronze (Table 1:Swarf a). This is consistent with published analyses of seventeenth-century bronze cannon (Tylecote 1992:112). A spot analysis of the metal confirmed the approximately 4% tin, but there was also about 3% arsenic present in the region of this analysis (Table 1:Swarf c). An approximately 10 micron square raster analysis of one of the inclusions showed a composition indicating mixed copper oxide and copper sulphide (Table 1:Swarf b) which would account for the slight variation in colour observed in reflected light.

Copper corrosion specimen

This was a flat rectangular strip about 310 mm long, 55 mm wide and about 9 mm thick. It had a 90° bend on one side where it was broken, and appeared to be folded over on the other side to form a double layer over a thin inner layer. It was encrusted with sand and a few embedded peppercorns, and had adhering small barnacles. It was a dark purple on one side, and a brownish green on the other. The fractured surfaces were also a deep blue and appeared coarsely granular to the unaided eye. The mass of this fragment was 443,9 g and it was not magnetic.

Optical examination of the polished section showed

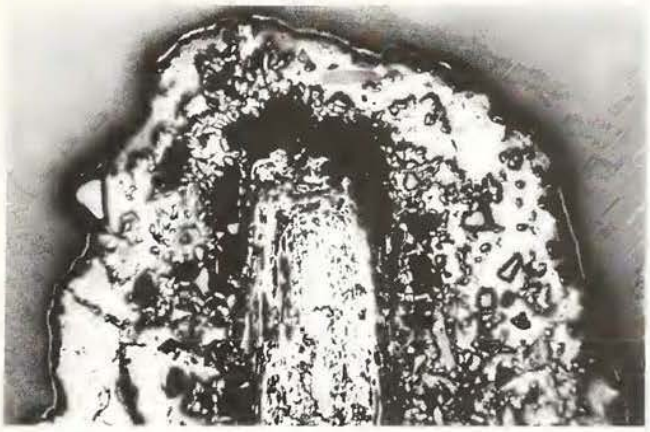

Fig. 11 Polished transverse section through the edge of the corroded sheet from the "Oosterland" showing the continuity of the corrosion layers (7,2 X).

Fig. 12 Micrograph of the altered core of the corroded from the "Oosterland" sheet showing an elongated grey inclusion (560 X).

that it consisted of six layers (Fig. 10), with the outer five consisting of corrosion product layers continuous over the end of the original plate (Fig. 11).

1. There was a core, about 0,5 mm thick, of fine covellite (CuS) crystals arranged in a chevron alignment, pointing towards the original edge of the plate. The covellite was identified from its very distinctive optical properties (Craig & Vaughan 1981:336). The covellite was present as platy crystals, with a characteristic whitish blue colour in air. The pleochroism under plane polarized light was blue to white and the anisotropy under crossed polarized light was orange to yellowish brown. This core contained numerous elongated lenticular inclusions with a white reflecting matrix crossed by acicular grey crystals (Fig. 12). These inclusions were about 10 microns across and difficult to locate under the SEM but the analysis of two of them indicated that they contained primarily lead and copper with significant antimony, arsenic, and strontium

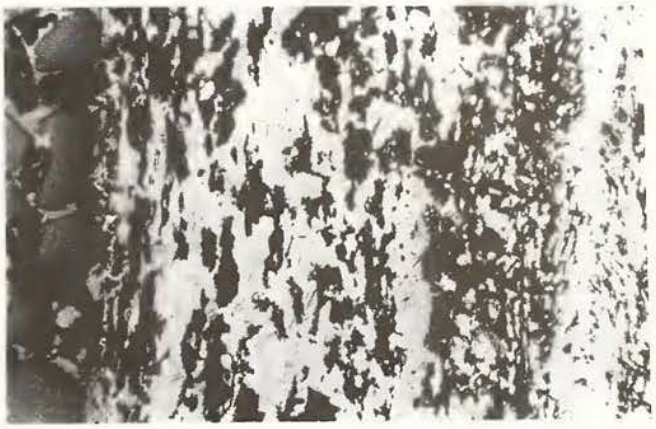

Fig. 13 Micrograph of the corroded sheet from the "Oosterland" showing the core (right) to the sandy layer 4 (left) (56 X).

(Table 1:Oost 1 a,b). There was a notable absence of sulphur in these inclusions. In reality they were probably oxides, but the EDS system used could not detect oxygen. This core represented the physical remains of the original copper plate, now completely corroded and transformed predominantly to covellite as a result of the chemical reaction of the copper with sulphur in the environment of burial.

2. The second layer, which completely surrounded the core, consisted of coarser covellite crystals with numerous irregular voids (Fig. 13). This layer was about 0,8 mm thick on each side of the specimen and contained a scatter of the inclusions present in the core. Layer 2 represented the primary corrosion product of the original plate represented by the core.

3. The third layer, concentric with layer two, was a discontinuous one, only about 100 microns thick. It contained bright, white reflecting, acicular crystals forming a line in the covellite matrix. These crystals were too small for individual analysis but a 5 micron by 5 micron square raster analysis and a spot analysis indicated similar compositions (Table 1:Oost1 c,d). The analyses of this layer contained predominantly copper and lead, with lesser amounts of sulphur, arsenic, and antimony, as well as traces of nickel, iron and strontium. The sulphur, and some of the copper, probably represented the covellite matrix between the acicular crystals. The lead, arsenic, and antimony was probably leached from some of the inclusions in the original copper plate as it corroded and were reprecipitated on the outer surface of the primary corrosion product.

4. The fourth layer, about 2,3 mm thick on each side of the specimen, consisted of more massive crystals of covellite and some blocky crystals of digenite

Fig. 14 Polished section through the copper rivet joining two sheets from the "Oosterland" (7,2 X).

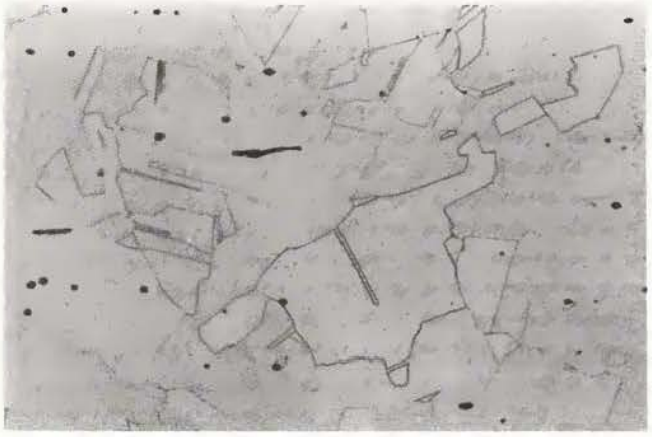

Fig. 15 Etched section of copper sheet from the "Oosterland" showing angular recrystallized grains with annealing twins (140 X).

Fig. 16 Etched section through the sheet (left) and rivet (right) from the "Oosterland" showing extreme grain deformation (140 X).

(Cu_9S_5). The latter was identified by its pale blue colour and isotropic behaviour under crossed polarised light. This layer also contained dense areas of sand grains, including detrital quartz as well as some unidentified calcareous microfossils. This layer formed part of an integument of secondary corrosion products which made up the bulk of the specimen.

5. The next layer was about 1 mm thick on each side of the specimen and consisted of massed covellite crystals with some digenite intergrowths.

6. The outermost layer was a thin layer of fine, columnar covellite, with the long axes of the individual crystallites perpendicular to the outer margin of the specimen.

Copper sheet specimen

This specimen consisted of a copper rivet joining two sheets of copper (Fig. 14). The rivet had a maximum diameter of 6 mm and a thickness of 4,5 mm. The sheets were 0,7-1,3 mm thick. This copper sheeting was well preserved and had regularly spaced holes along one edge. The sheet was not magnetic.

The metallographic section showed that the rivet and the plates were made of optically similar materials. The average grain size was about ASTM 5-7. All the components had been cold-worked, annealed and recrystallised, as evidenced by the angular recrystallized copper grains with characteristic annealing twins (Fig. 15). These are indicative of cold-working followed by heating to above about 300°C (Maddin, Wheeler & Muhly 1980). The annealing was probably to soften the sheet after beating it out and before final shaping. All the components had suffered some cold-work after the anneal. The degree of grain deformation at the top of the rivet showed that it was more heavily cold-worked than the bottom face and the core of the rivet had very little residual cold-work strain. The margins of the rivet and the joined sheet were severely deformed (Fig. 16) by cold work during the emplacement of the rivet. The Knoop microhardness of the core of the rivet was $H_K = 96$ (50 g load, 15 s, range 88-101, $n = 5$) [adjusted value = 88]. The Knoop microhardness of the annealed sheet was $H_K = 94$ (50 g load, 15 s, range 83-98, n = 5) [adjusted value = 86] (cf. Vickers microhardness of pure copper, worked and annealed $H_V = 50$ to 60; pure copper, cold worked $H_V = 100$-120 (Scott 1991:82).

The bulk EDS analysis of the core of the rivet over a 1 mm by 1 mm square area indicated no detectable elements other than copper. The same was true of a spot analysis of the metal in the plate (Table 1:Oost2 a,b).

The rivet had a slightly higher density of inclusions than the sheet but they all had similar appearances. There were very sparse inclusions consisting entirely of cuprite (Cu_2O), identified by its characteristic blue colour and red internal reflections (Craig & Vaughan 1981). There were also rare, elongated, dark blue inclusions without any internal reflections. These were probably copper sulphides. The most numerous inclusions were rounded, or elongated glass inclusions, many with included droplets of cuprite (Fig. 17). The glass appeared crumbly

Fig. 17 Polished section through copper rivet from the "Oosterland" showing glassy inclusions containing cuprite globules (280 X).

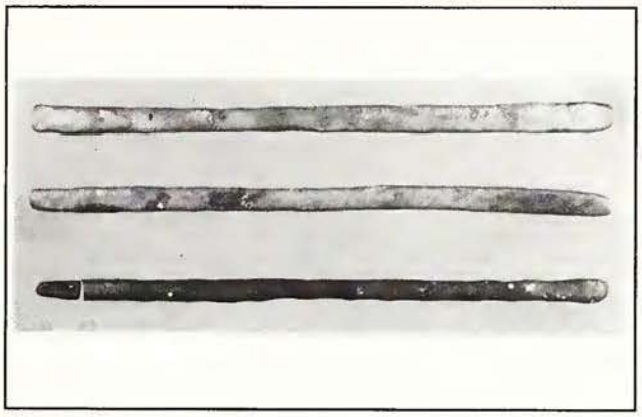

Fig. 18 Photograph of three copper trade bars from the "Waddingxveen" (maximum length 240 mm).

under interference contrast and had bright white internal reflections under crossed polarised light.

A spot analysis of a cuprite inclusion detected nothing but copper (Table 1:Oost2 c), but spot analyses and small raster analyses of the glassy inclusions (to take into account the possible inhomogeneity of the glass) showed compositions dominated by lead, with considerable copper, and significant arsenic, antimony, and strontium (Table 1:Oost2 d-h). These elements were present in generally similar proportions as the same elements in the elongated globular inclusions in the core of the corroded sample (Table 1:Oost1 a,b). The inclusions in the copper were glassy and probably represented mixed copper/lead oxides quenched to a glass.

Copper bar

Three copper bars recovered from the "Waddingxveen" were available for study. One had already been sampled for EDS analysis by Robert Knutsen, Department of Materials Engineering, University of Cape Town. A further sample was removed from this bar for metallographic investigation.

The bars were oval in cross-section, slightly flattened on one side and appeared to have been cast into round-bottomed open moulds (Fig. 18). The unsampled bars varied slightly in mass and dimensions (Table 2) and obviously were not cast in identical moulds.

Table 2. Mass and dimension of the copper bars.

MASS (g)	LENGTH (mm)	WIDTH (mm)	THICKNESS (mm)
89,6	210	10	6-8
120,2	235	10-12	6-8
112,6	240	10-12	5-7

In section the sampled bar had a thin external rind of secondary cuprite and other oxidation products. There was some casting porosity, particularly near the middle of the bar (Fig. 19). The central voids were accompanied by irregular glassy inclusions often forming thin stringers between the central copper grains. The metal itself consisted of rounded dendritic grains of cast copper with blue globules of cuprite on the grain boundaries (Fig. 20; *cf.* Brooks 1982:fig. 8-3). Bulk raster analyses showed about 99 % copper with minor sulphur and silcon (Table 1:Bar a,b). A spot analysis of the interior of a copper grain showed no detectable alloying elements. The inclusions consisted of cuprite (Cu_2O) with minor sulphur and in some cases iron and arsenic (Table 1:Bar c-f). The Vickers microhardness of the copper grains was HV 54,9 (200 g, 10 s, n = 5, range 47,25-65,41) and their grain size was approximately ASTM 5.

This bar consisted of so-called tough pitch copper, a Cu-O alloy with about 0,05% oxygen (Brooks 1982), in the as-cast state. It represents a primary copper product which has not undergone deoxidizing or other refining.

JB1 "Bato"

This sample was from the identified wreck of the Dutch warship "Bato" (1806). The sawn specimen measured 8 mm by 12 mm in maximum cross section and had a mass of 1,41 g. It was not magnetic.

Optical examination of the section etched with an alcoholic $FeCl_3$ solution showed that it consisted of a single phase bronze, with a cored dendritic structure typical of a slowly cooled casting. The bulk was very porous and had not been annealed. Slip banding in some of the grains was evidence of residual cold work. The bulk composition contained just under 3% tin and a small but detectable amount of lead (Table 1:analysis JB1 a).

i. In the electron microscope the lead inclusions were visible as small bright spots trapped between the dendritic arms.

ii. There were also globular to elongated non-etching blue inclusions which consisted of a copper sulphide (Table 1:analysis JB1 b), close in composition to chalcocite (Cu_2S), a common inclusion in copper-based alloys.

iii. There were very sparse irregular light blue inclusions with even lighter reticulations of an exsolved phase.

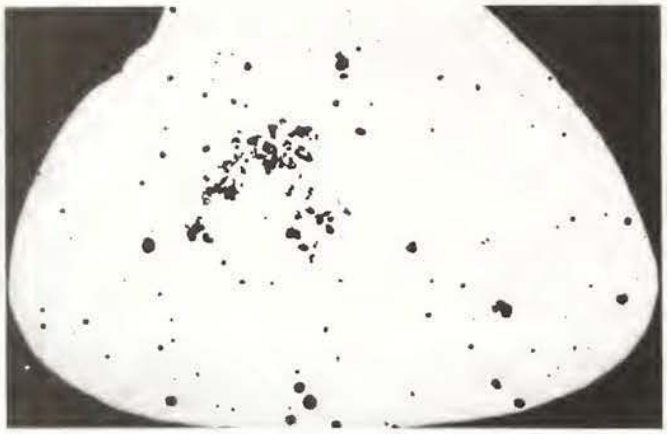

Fig. 19 Polished transverse section of a copper trade bar from the "Waddingxveen" showing casting porosity (7,2 X).

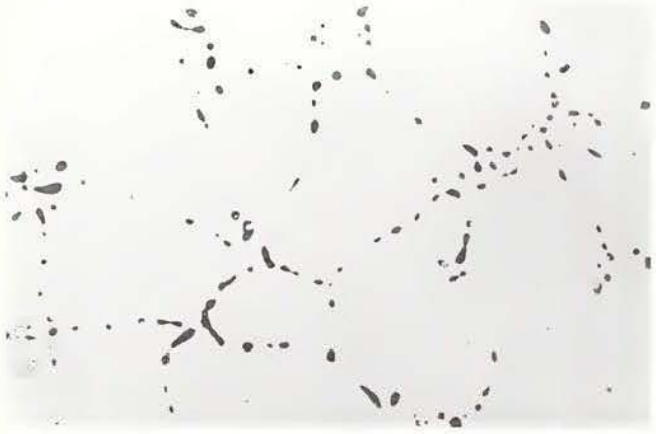

Fig. 20 Polished section of a copper trade bar from the "Waddingxveen" showing rounded copper grains with cuprite droplets on the grain boundaries (224 X).

iv. Very sparse dark blue-grey inclusions had bright internal reflections under crossed polars. These may have been a copper oxide glass or a transparent mineral such as sphalerite (ZnS).

JB2 "Brunswick"

This sample was from the identified wreck of the "Brunswick", a British East Indiaman wrecked in 1805 (J. Boshoff pers. comm.). The sawn pyramidal specimen measured 6 mm by 10 mm in maximum cross section and had a mass of 0,94 g. It was not magnetic.

Optical examination of the section etched with an alcoholic $FeCl_3$ solution showed that it consisted predominantly of a single phase bronze, with a cored dendritic structure typical of a slowly cooled casting. The bulk was very porous and had not been annealed. There was no evidence of cold work. The bulk composition contained 5,5% tin and nearly 1% lead (Table 1:analysis JB2 a).

i. The lead inclusions were visible as bright spots under the electron beam.

ii. Numerous, blue globular inhomogeneous droplets consisted of two phases. The major component was a copper sulphide with a composition approximating that of chalcocite (Cu_2S) with a small iron impurity (Table 1:analysis JB2 b), and the minor component had the composition of sphalerite (ZnS) (analysis not recorded).

iii. Characteristic complex multiphase inclusions were common. These consisted of various crystalline Cu/Sn phases associated with irregular droplets of lead. All of the components of these inclusions were inhomogeneous. Under the electron beam the brightest phase proved to be predominantly lead (analysis not recorded). The intermediate grey phase contained a darker eutectic exsolution but had a bulk composition indicating a 23% tin bronze (Table 1:analysis JB2 c), corresponding in composition to the high temperature beta phase (Scott 1991). The darkest phase in the electron image consisted of blocky inhomogeneous crystals with a tin content slightly lower than that of the bulk bronze matrix (Table 1:analysis JB2 d). This phase was light pinkish yellow under plane polarised light, and on etching stained a honey brown. These were low tin copper.

iv. There were very sparse grey-blue single phase inclusions with bright internal reflections under crossed polarised light. These were probably single crystals of sphalerite.

JB3 Unidentified

This sample was submitted without identification to act as a control check on the identification procedures. The sawn specimen measured 8 mm by 14 mm in maximum cross section and had a mass of 1,11 g. It was not magnetic.

Optical examination of the section etched with an alcoholic $FeCl_3$ solution showed that it consisted of a single phase bronze, with a cored dendritic structure, largely recrystallised by annealing. There was considerable evidence of cold work in the form of slip bands within the crystals. The specimen was severely corroded and etched far more rapidly than the other three. The porous bulk had a composition containing about 4% tin and 1% lead (Table 1:analysis JB3 a).

i. There were numerous opaque dark grey globules, without internal reflections.

ii. Sparse light blue two phase inclusions were associated with pinkish brown cuboids which etched honey brown. These cuboids, representing low tin copper crystals, surrounded many of the voids. They may have been the result of selective leaching of tin from the exposed metal around the porosities.

JB4 Rudder

This sample was from the disassociated rudder, and

Fig. 21 Cored dendritic structure of the rudder sample JB4 after etching for 10 seconds in alcoholic $FeCl_3$ solution. The inclusions tend to occupy intersticies between the dendritic arms (50 X).

Fig. 22 Complex inclusions in the rudder sample JB4 (280 X).

the identification of its provenance was the main object of the investigation. The sawn specimen measured 4 mm by 17 mm in maximum cross section and had a mass of 0,70 g. It was not magnetic.

Optical examination of the section etched with an alcoholic $FeCl_3$ solution showed that it consisted predominantly of a single phase bronze, with a cored dendritic structure typical of a slowly cooled casting (Fig. 21). The bulk was porous and had not been annealed. There was no evidence of cold work. The bulk composition contained 5% tin and about 0,5% lead (Table 1:analysis JB4 a). In appearance it was very similar to Sample JB2.

i. Dark blue globular inhomogeneous droplets consisted of two phases, the darker of which had bright red internal reflections in crossed polarised light. These were probably cuprite.

ii. There were numerous single phase dark grey-blue inclusions with bright internal reflections.

iii. The characteristic complex multiphase inclusions consisted of various crystalline Cu/Sn phases associated with irregular droplets of lead, and cuboid pinkish brown tin-poor copper crystals (Fig. 22).

iv. In the SEM free lead inclusions were visible as small bright spots trapped between the dendritic arms.

DISCUSSION AND CONCLUDING REMARKS

The analysis of the metallic sample showed that the "Oosterland" cannon was made of an unremarkable bronze alloy with approximately 3,5% tin and a minor amount of lead. The only sample for comparison from the Cape consists of the drill turnings from the unidentified bronze cannon housed at the Cape Town Castle. The Castle cannon was made of a 4% tin bronze, consistent with published analyses of seventeenth-century bronze cannon (Tylecote 1992:112). This cannon did not appear to contain lead, but about 3% arsenic was detected, and the inclusions consisted of mixed copper oxide and copper sulphides.

Very few conclusions can be drawn from comparative analysis of only two samples. It is therefore recommended that in future samples should be taken systematically from other bronze cannon and large military hardware of the Dutch VOC period to characterise the range in variation in the material used and to determine any temporal trends or variations in application.

The analysis of the cannon corrosion product from the second "Oosterland" cannon records something of its post-burial history. The macroscopic layering, with varying densities of sand, point to a fluctuating chemical and physical environment, possibly with successive episodes of burial and exhumation. Unfortunately a sample of the original metal was not available for analysis. It would have been interesting to compare the chemistry of the metallic droplets in the corrosion product with that of the inclusions in the parent bronze.

The chemical analysis of the inclusions in the copper corrosion product confirmed its identity with the uncorroded strips. The inclusions in the corrosion sample did not appear to be fully glassy although their chemical composition was very similar to the glassy phases in the copper. Presumably, the corrosion of the copper allowed the unstable glassy components of the inclusions to react, partially devitrify, and recrystallize to produce the acicular grey crystals observed in the brightly reflecting matrix. The chemical similarity of the glassy phase in the copper sheets and the residual inclusions in the corroded strip leaves no doubt that the latter is a severely corroded fragment of copper sheeting.

The extreme difference in the degree of corrosion is provocative. Obviously, under the circumstances of marine burial copper sheeting can survive virtually uncorroded for many hundreds of years. But in the case of this sheeting part of the material was in very close proximity to a plentiful supply of sulphur to provide the

reactant to produce covellite. It is known that copper sheeting was often used to line rooms in the vicinity of the gunpowder room to minimise the risk of fire (B. Werz pers. comm.). When the ship sank, the rupture of barrels of ready mixed gunpowder or of raw sulphur may have created localised concentrations of sulphur on the copper cladding. If these concentrations were not dispersed by current action then they would have provided suitable chemical conditions for the selective reaction and corrosion of some of the copper sheets and cladding strips.

This would have required locally stable post-depositional conditions which is borne out by the morphology of the corrosion products. Reaction of the copper with the sulphur would proceed at the margins of the metal sheet (layer 3), slowly trapping sand grains (to build layer 4) as well as invading the corroding metal which expanded with the progressive in situ crystallisation of corrosion products (layer 2) until corrosion reached the core (layer 1). The immediate environment was enriched with copper leached from the corroding metal and this enabled nearly pure, large crystals of covellite to crystallise slowly on the outside of the trapped sand grain layer, incorporating peppercorns and other debris in the process (in layers 5 & 6).

The metallographic study of the copper bar ingot was not particularly revealing and in itself tells us nothing about its possible provenance. The trace element study conducted at the British Museum identified the source of the copper bar as Japan (P. Craddock pers. comm.). This is not surprising because the "Waddinxveen" was known to have been on its return voyage from the Far East (B. Werz pers. comm.).

The study of the bronze rudder samples pointed to the "Brunswick" as the origin of the disassociated rudder. The physical structures and bulk chemical analyses of these four samples were very similar. They were all leaded, low tin bronzes, with cored dendritic structures. Two samples showed evidence of cold work and one had been annealed, but this was due to fabrication and was not an intrinsic identifying characteristic.

Sample JB3 look superficially distinct under the microsocope because of its being severely corroded, containing more numerous internal voids, having more plentiful tin-poor copper-rich areas, and etching more rapidly than the other three samples. In terms of the inclusion suite sample JB1 (from the "Bato") was distinct, with far fewer of the complex light blue inclusions and no associated pinkish cuboid crystals. Samples JB2 and JB4 are closest to each other in appearance, but JB2 lacks the numerous blue-grey inclusions with bright internal reflections which are numerous in JB4. Apart from these differences, samples JB2, JB3 and JB4 had similar suites of inclusions and on the basis of this observation the highest probability is that the rudder is associated with the wreck of the "Brunswick".

Three of the four bronze samples were very similar in bulk composition, but had subtle differences in their inclusion suites. The minor differences in tin and lead content could be due to large scale inhomogeneity in the large castings from which these samples were taken, or slightly different bronze compositions may have been used for different components on any individual vessel. This could also explain the differences in inclusion suites in samples JB2-4. JB1 appeared to be distinct both in terms of chemical composition and inclusions and bears the least resemblance to the rudder.

The archaeometallurgical studies reported here are the first addressing various problems of identification and interpretation on maritime material from the Cape. As such, these are preliminary investigations, but they illustrate something of the range of questions that can be addressed with standard metallurgical techniques. The analysis of the bronze cannons initiates what hopefully will become a growing body of data about the composition of early colonial metals brought to and used at the Cape. The study of the corroded copper strips, not only identified them for what they were, but provided insight into the storage and structural arrangements of the vessel. The association of the detached rudder with the "Brunswick" would not have been possible without the detailed analysis of the inclusions in its bronze components. And the trace element analysis of the copper bar, although not reported here in detail, enabled staff at the Department of Scientific Research at the British Museum to identify the source of the copper as Japan.

ACKNOWLEDGEMENTS

My thanks are due to Dr Bruno Werz (University of Cape Town) and Mr Jaco Boshoff (Maritime Museum, Cape Town) who generously gave me access to the samples, gave me permission to publish the analyses in this paper, and read and commented constructively on the draft. I thank Prof A. Ball for access to the microhardness tester in the Department of Materials Engineering, UCT and Dr R. Knutsen of that department for giving us a copy of the results of his analysis of the copper bar. Mr D. Gerneke of the Electron Microscope Unit, UCT provided assistance with the scanning electron microscopy. The Department of Archaeology, UCT provided research facilities and administrative support under the auspices of Prof N.J. van der Merwe. Financial support from Anglo-American De Beers Chairman's Fund Educational Trust, the Foundation for Research Development, and the Centre for Science Development for research into early mining and metallurgy is acknowledged with gratitude. Opinions expressed in this paper and conclusions arrived at are those of the author and not necessarily to be attributed to any of the supporting agencies.

REFERENCES

ASTM 1981. Standard methods of estimating the average grain size of metals. ASTM Standards - Part II, E 112:186-220. Philadelphia: American Society for Testing and Materials.

Brooks, C.R. 1982. Heat treatment, structure and properties of nonferrous alloys. 1-420. Ohio: American Society for Metals.

Craig, J.R. & Vaughan, D.J. 1981. Ore microscopy and ore petrography. 1-406. New York: John Wiley & Sons.

Maddin, R., Wheeler, T.S. & Muhly, J.D. 1980. Distinguishing artifacts made of native copper. Journal of Archaeological Science 7:211-225.

Ross, J.D.J. 1985. Indentation hardness of crystalline solids at low loads. Unpublished Ph.D. thesis: University of Exeter.

Scott, D.A. 1991. Metallography and microstructure of ancient and historic metals. 1-155. Los Angeles: J. Paul Getty Trust.

Snyman, L.W. 1989. Optimum use of Nomarski light microscopy in the characterization of semiconductor devices. South African Journal of Science 85:698-701.

Tylecote, R.F. 1992. A history of metallurgy. 1-205. London: The Institute of Metals.

Werz, B.E.J.S. 1989. Saving a fragment of the underwater heritage; a multi-faceted approach. Cabo. Yearbook of the Historical Society of Cape Town 4(4):13-17.

Werz, B.E.J.S. 1992. The excavation of the 'Oosterland' in Table Bay: the first systematic exercise in maritime archaeology in southern Africa. South African Journal of Science 88:85-89.