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Rooswijk, Protected Wreck Site, Goodwin Sands Conservation of copper alloy artefacts from the Dutch East Indiaman the Rooswijk

Elisabeth Kuiper

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ROOSWIJK
PROTECTED WRECK SITE
GOODWIN SANDS

CONSERVATION OF COPPER ALLOY ARTEFACTS FROM THE DUTCH EAST INDIAMAN THE ROOSWIJK

Elisabeth Kuiper

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SUMMARY
This report summarises the investigation, conservation cleaning and analysis of three different copper alloy artefacts from the Rooswijk shipwreck prior to desalination.

CONTRIBUTORS
The initial conservation assessment was carried out under the supervision of Eric Nordgren, project conservator for the Rooswijk project. Angela Middleton oversaw the work presented here.

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INTRODUCTION

During the summer of 2017 a maritime archaeological excavation on a 17th century shipwreck was carried out on the Goodwin Sands off the coast of Deal in Kent, England. The project was both initiated and funded by the Dutch state's Cultural Heritage Agency, as the shipwreck was known to be that of the Dutch East Indiaman called the 'Rooswijk'. The protected wreck is currently on Historic England's Heritage at Risk Register (HAR), and faces declining conditions with major localised problems.

MSDS Marine Ltd managed the project, including collaboration between a wide range of stakeholders. Key stakeholders included Historic England, who partnered for the project and contributed staff and facilities.

Over 1800 objects were found, including part of the cargo, equipment and possible personal artefacts. Amongst the equipment were three copper alloy objects: a cauldron, a pan and a lid.

This study reports investigations into their construction, the manufacturing processes involved, alloy composition and conservation state.

All objects were studied visually and through x-radiography for notable features or hammer marks indicating manufacturing processes. Investigative cleaning took place both in order to study surface features and to inform the subsequent desalination process. If necessary the artefact was strengthened and consolidated in order to give it stability and improve handling.

INVESTIGATION AND CONSERVATION

RK17 A01137 – Cauldron

Assessment

The cauldron consists of a basin completed with a round rim. Lugs are attached on opposite sides, which hold a handle in place (Fig 1). On the lower face of side D a separate riveted feature is clearly visible (Fig 5). This could have served as a reinforcement to attach a leg, making this cauldron a three legged cooking pot.

The cauldron is in a fragmentary and therefore fragile state (Fig 1-5). Cracks can be seen to run through the material and large parts of the object are missing. The rim, which seems otherwise complete, has broken. This part needs support in order to prevent further damage. The wall of the cauldron is very thin, about a millimetre thick. Pieces along the edges run a risk of breaking off during handling as small fractures run all along the edges and into the material.

In the bottom of the cauldron sediment is concreted to the surface (Fig 1). The sediment contains small pebbles and shells. Concreted iron corrosion is adhered to the surface on side C of the cauldron (Fig 4 and 5). The overall surface of the object is red brown with local light green staining. In some areas brighter green corrosion spots are visible, especially in small areas on the handle.

Fig 1: Top view of object RK17 A01137: before conservation; with viewpoints for subsequent object photos.

Fig 2: View from side A of object RK17 A01137: before conservation.

Fig 3: View from side B of object RK17 A01137: before conservation.

Fig 4: View from side C of object RK17 A01137: before conservation.

Fig 5: View from side D of object RK17 A01137: before conservation.

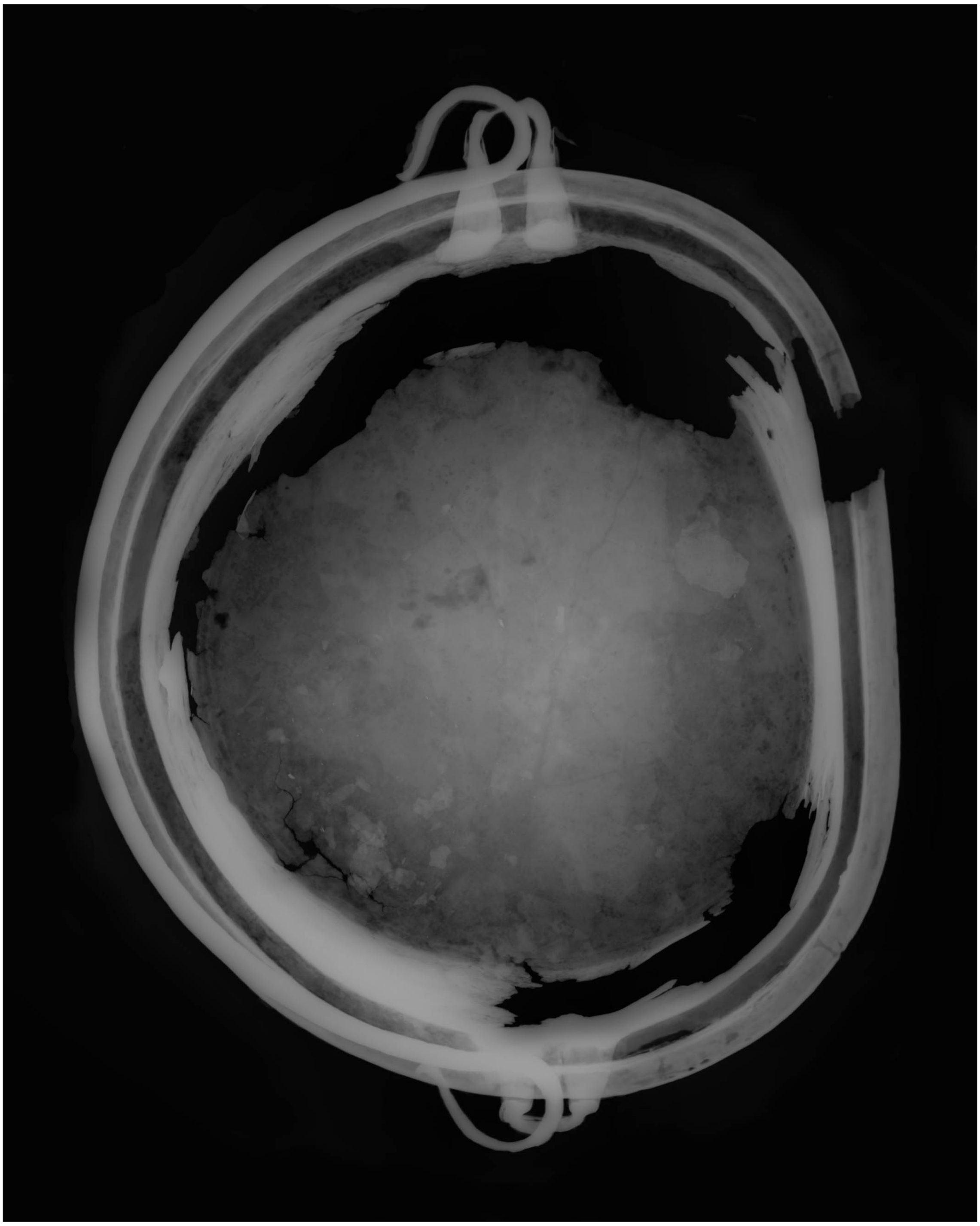

Fig 6: X-radiograph showing top view of the object RK17 A01137 (P4476-4479, kV: 100, mA: 3, exposure time in sec.: 1.5).

Investigation

X-Radiography

The entire object was studied by X-radiography in order to create a record of the current state of preservation and to see if any unusual or otherwise invisible features could be found (Fig 6). The object was studied both from above and from the sides.

No maker's mark or hammer marks were found in the material. Fractures could be seen to run into the metal at various points (Fig 7). In particular, the joints of the riveted feature and the metal loop were investigated (Fig 7 and 8). It is clear that the lugs, as well the reinforcement plate, are riveted to the cauldron wall.

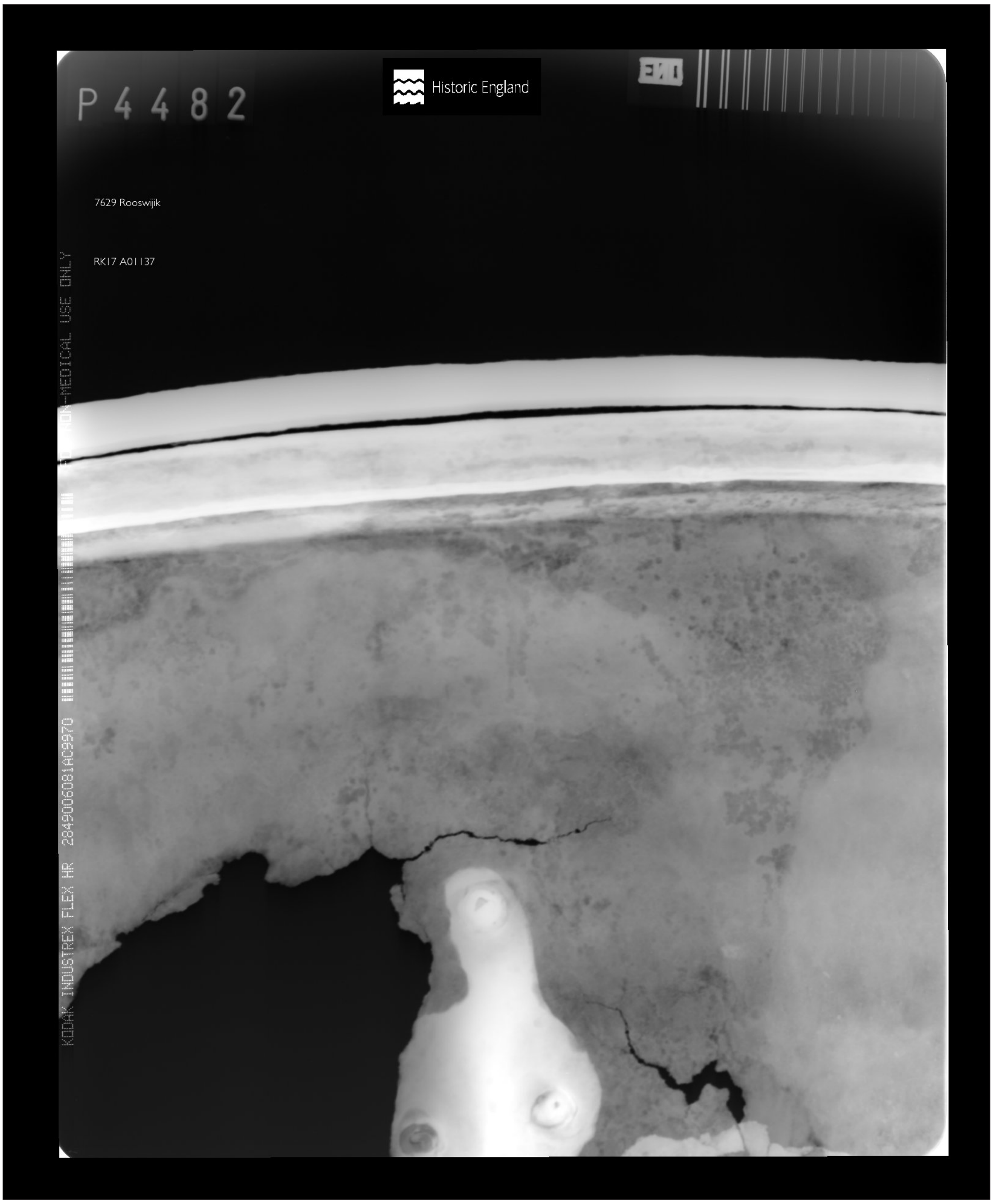

Fig 7: X-radiograph showing riveted feature on object RK17 A01137 (P4480, kV: 80, mA: 3, exposure time in sec.: 2.5).

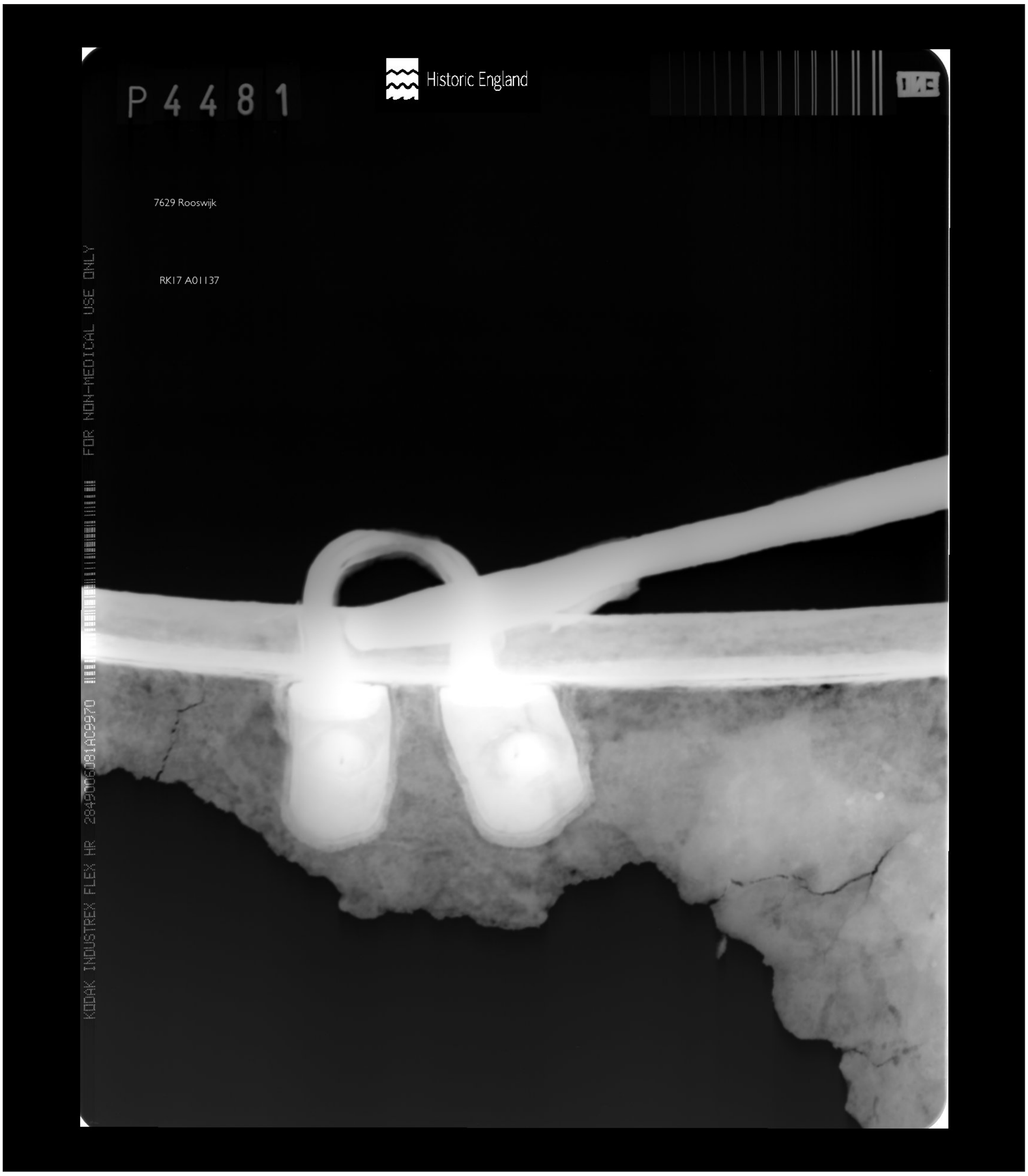

Fig 8: X-radiograph showing loop and handle of object RK17 A01137 (P4481, kV: 100, mA: 3, exposure time in sec.: 2.5).

X-Ray Fluorescence

The composition of the cauldron was studied by handheld X-ray fluorescence spectrometry (pXRF). As it consists of different elements, like the basin, two lugs and a handle, multiple areas were analysed.

The objects were examined using a portable X-ray Fluorescence (pXRF) spectrometer (a Niton XL3t). Spectra were collected using the 'Cu/Zn mining' pre-set method for a total of 45 seconds (sec) per analysis:

Cu/Zn Mining

Light (5 sec):	Mg, Al, Si, P, S
Low (5 sec):	K, Ca, Ti, V, Cr
Main (20 sec):	Mn, Fe, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Zr, Nb, Mo, Hf, Ta, W, Re, Au, Pb, Bi, Bal
High (15 sec):	Pd, Ag, Cd, Sn, Sb, Ba

Both the lugs and handle were found to consist almost entirely of copper (98 wt% Cu) with traces of lead (0.7 wt% Pb), zinc (0.6 wt%) and antimony (0.5 wt% Sb).

The composition of the body of the cauldron versus that of the rim appeared to be more difficult to interpret as the results yielded some variability in lead and tin between the two. In spite of this, the body of the vessel and the rim are assumed to consist of the same metal alloy; neither the x-radiographs nor visual examination give any indication that the rim is soldered on or otherwise separately attached to the basin. The measurements of copper from the body of the vessel and those from the rim do correspond and give approximately 68 wt% Cu. The weight percentage of zinc as measured in the basin is approximately 23.5 wt% Zn. On the rim a somewhat higher percentage is measured of about 31.5 wt%. Additionally, more lead is measured in the basin (7.2 wt% Pb) than on the rim (0.8 wt% Pb). The basin also shows about 3.5 wt% tin (Sn) and just 0.1 wt% Sn on the rim. This alloy is commonly referred to as brass.

The reason for the difference in lead and tin present on the surface of the object could result from corrosion processes. pXRF measures the surface of the object and cannot penetrate the metal further than micrometres. The surface of the object is where the metal is most susceptible to corrosion, for example in the form of dezincification or destannification. Another possibility is that the basin was once tinned.

Conservation

In order to offer the object better support during handling as part of the desalination process, an external reinforcement was built. In addition to the external support, insecure fragments along the edges of the material were consolidated to ensure their stability. Concreted corrosion layers were also removed from the surface of the object. In order to prepare the object for these treatments, it was turned over and fitted onto a specially made support of polystyrene foam.

As a first step, concreted corrosion layers were cleaned from the internal and external surface of the object to offer better access to the surface of the object when building the support. Removing these corrosion layers also helps in the desalination process. Concretion layers were removed using a pneumatic air-scribe. To ensure that no layers were removed that were originally part of the object itself, attention was paid to so-called ‘external markers’ like stones and shells encapsulated in the corrosion crust.

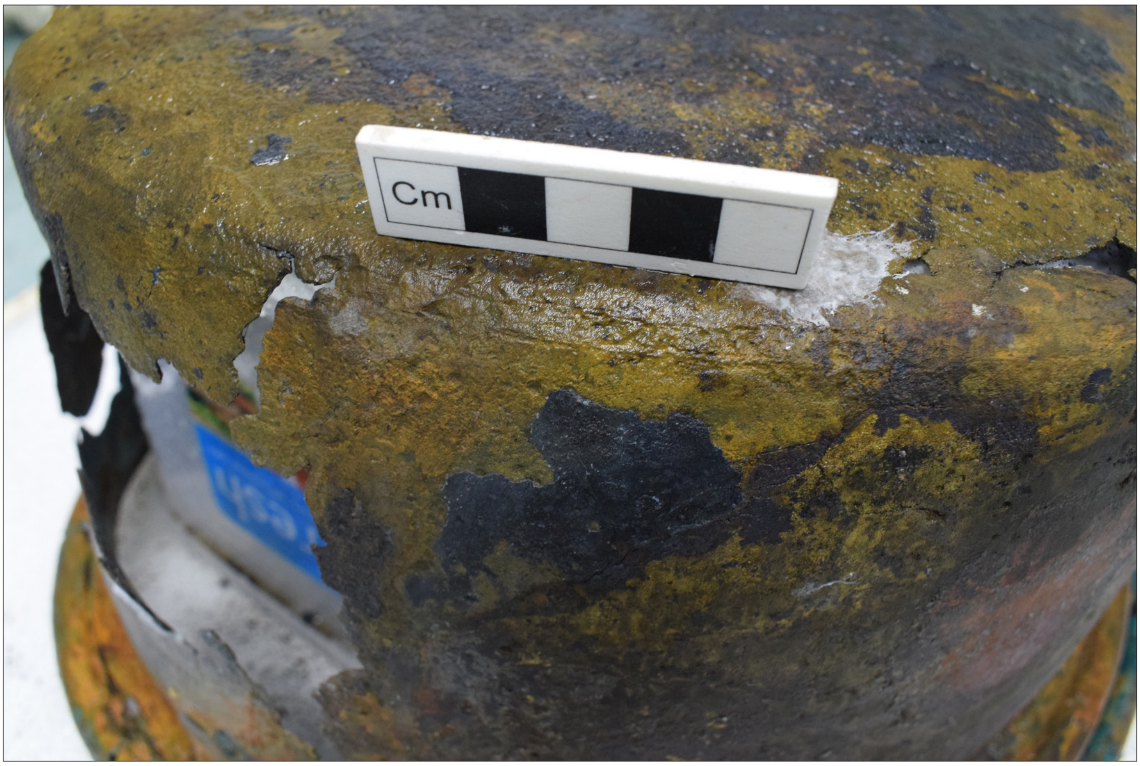

Fig 9: Incision lines on the outer surface of the cauldron.

During cleaning of the object a feature was revealed: two small incision lines were found to run along the external wall of the cauldron (Fig 9). Possibly these were decorative or created during the manufacturing process; as the lines are located on the edge of the wall. They might have been used as an indication for the metalworker on the placement of the wall of the cauldron.

Some areas, with long cracks and minimally adhered fragments required consolidation. These areas were dried temporarily with acetone. Subsequently, a layer of Japanese tissue paper soaked in Paraloid B72 in acetone was applied over the fractures. In total thirteen places were reinforced in this manner. The X-radiographs were used to locate fractures and insecure areas as seen in Figs 10 and 11.

A support cradle for the entire cauldron was made out of X-Lite Classic sheets (Fig 12). This material consists of natural mesh cotton fabric impregnated by an aliphatic polyester (polycaprolactone) based polymeric solution. These solid, white, flat sheets are insoluble in water and transition from a rigid, solid state to a soft rubber-like material at a temperature of ca. 50^0C. When heated, the sheets can be formed onto a pre-existing shape; they set when cooled down and retain this form. This process was carried out on the cauldron with a layer of tin foil in between the object and the sheets to prevent the soft material from adhering to the surface of the object.

Fig 10: Object RK17 A01137 during conservation with two areas where Japanese tissue paper was applied.

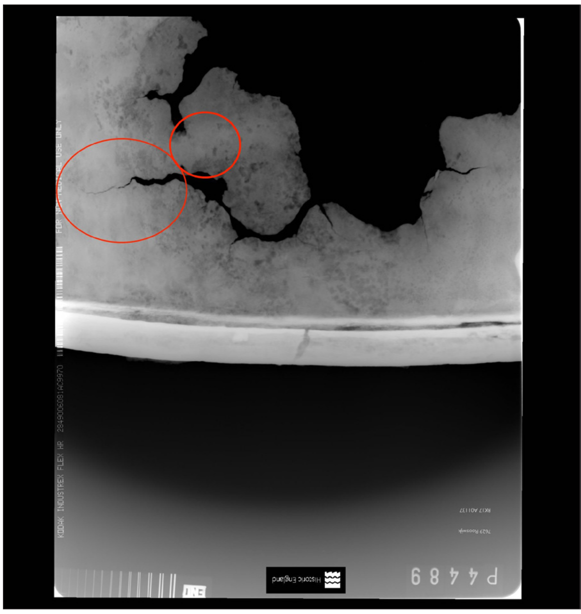

Fig 11: X-radiograph showing fractures running into material of object RK17 A01137 (P4489, kV: 100, mA: 3.5, exposure time in sec.: 2.5); red circles showing areas were Japanese tissue paper was applied.

Fig 12: Object RK17 A01137 during conservation with external X-Lite support in place.

RK17 A01294 – Pan

Assessment

Object RK17 A01294 is a heavily concreted artefact with pieces of glass, shells and stones encapsulated in the concretion layers. The general shape of the object is round, but the encrusted corrosion layers concealed its true shape. In one area on the rim the object could be made out, demonstrating the thick corrosion crust (see lower left hand corner in Fig 13).

The colour and composition of the thick concretion layer suggested it mainly consisted of iron corrosion. The origin of the iron corrosion is at this stage unknown. The artefact itself was assumed to consist of a copper alloy.

Fig 13: Object RK17 A01294 before conservation.

Investigation

X-Radiography

The object was studied by X-radiography. No fractures in the material or maker's marks were discovered. The metal appeared solid but covered by a layer of concreted iron corrosion. At four successive places small, round features showed in the X-radiograph. These were thought to relate to construction and likely to be rivets.

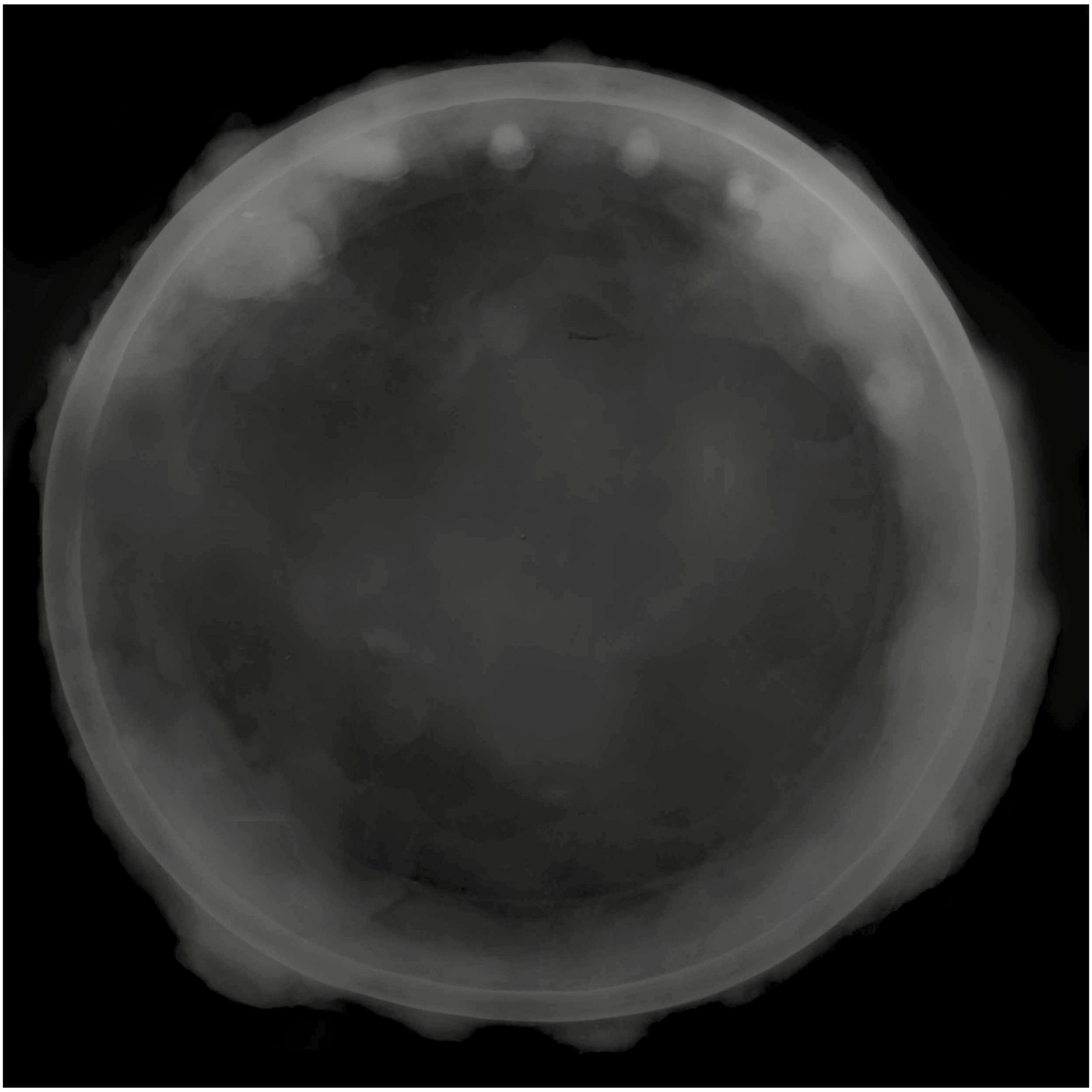

Fig 14: X-radiograph showing top view of the object RK17 A01294 (P4466-4469, kV: 210, mA: 5, exposure time in sec.: 3); possible riveting visible as denser spots on upper side image.

X-Ray Fluorescence

The material composition of the pan was studied using pXRF in four different areas following cleaning (Fig 15 and 16. The copper alloy of the pan itself was analysed on two different places: on the base of the pan and on the rim. The analysis gave a clear result showing a copper alloy of approximately 66wt% Cu, 27wt% Zn, 2.3wt% Pb with traces of As and Ni. This composition is commonly referred to as brass. The rivets, as will be shown next, were on the other hand made from copper.

The rivets were analysed in two different places showing they are almost entirely made out of copper. The analyses suggests a composition of 97wt% Cu, 0.8wt%Pb, 0.4wt% Zn with possible traces of As and Ni.

Traces of iron (Fe) were also found in varying quantities. It is unclear if these traces are related to the alloy or to iron contamination due to the iron corrosion crust on the object's surface.

Fig 15: Top view obverse side of object RK17 A01294 after corrosion removal.

Fig 16: Top view of reverse side of object RK17 A01294 after corrosion removal.

Conservation

Corrosion layers and sediment were cleaned from the surface of the dish using a pneumatic air-scribe. The main corrosion products on the surface of the object seemed to be concreted iron corrosion together with sediment. Although the origin of the iron corrosion product could not be determined it was clear that the original surface lay underneath. In one area the surface of the object could be seen underneath the corrosion layer and this was used to guide the cleaning of the object. The external markers like stones and shells confirmed this. The features that were seen earlier on the X-radiograph were found to be copper rivets (see above). On the inside of the pan the rivets are flattened, but on the outside they protrude from the surface of the object (Fig 17 and 18). The square rivets stick out about 1 cm and end in a flat head. Possibly they would have held an iron handle in place, which would also explain the concreted iron covering the object. In most areas the corrosion did not adhere to the surface of the object much, but near the rivets the iron corrosion was somewhat more solid. Despite this it was not possible to conserve this potential iron component as it was mineralized in such a manner that no remains could be kept in place.

Fig 17: Object RK17 A01294 after corrosion removal showing rivets on the inside of rim.

Fig 18: Object RK17 A01294 after corrosion removal showing rivets on the outside of rim.

RK17 A01073 – Lid

Assessment

One of the artefacts from the Rooswijk is a large lid. The lid consists of a round sheet metal that has been folded over a round metal hoop.. The hoop was created from a metal strip made into a circle and riveted together at the ends g (Fig 19). On top of the lid, a handle likely also to be attached to the lid with rivets was obscured by layers of concreted sediment (Fig 20).

The entire object seems to consist of a copper alloy as typical superficial reddish brown and green corrosion layers can be seen on the surface (Fig 21 and 22). In some local areas sediment has adhered to the surface of the object and can be found around rivets and under folds in the metal.

The object is broken and incomplete. The top is detached from the hoop in multiple areas and along these edges the metal can be seen to be very fragile and deformed. The material has long fractures running into the metal.

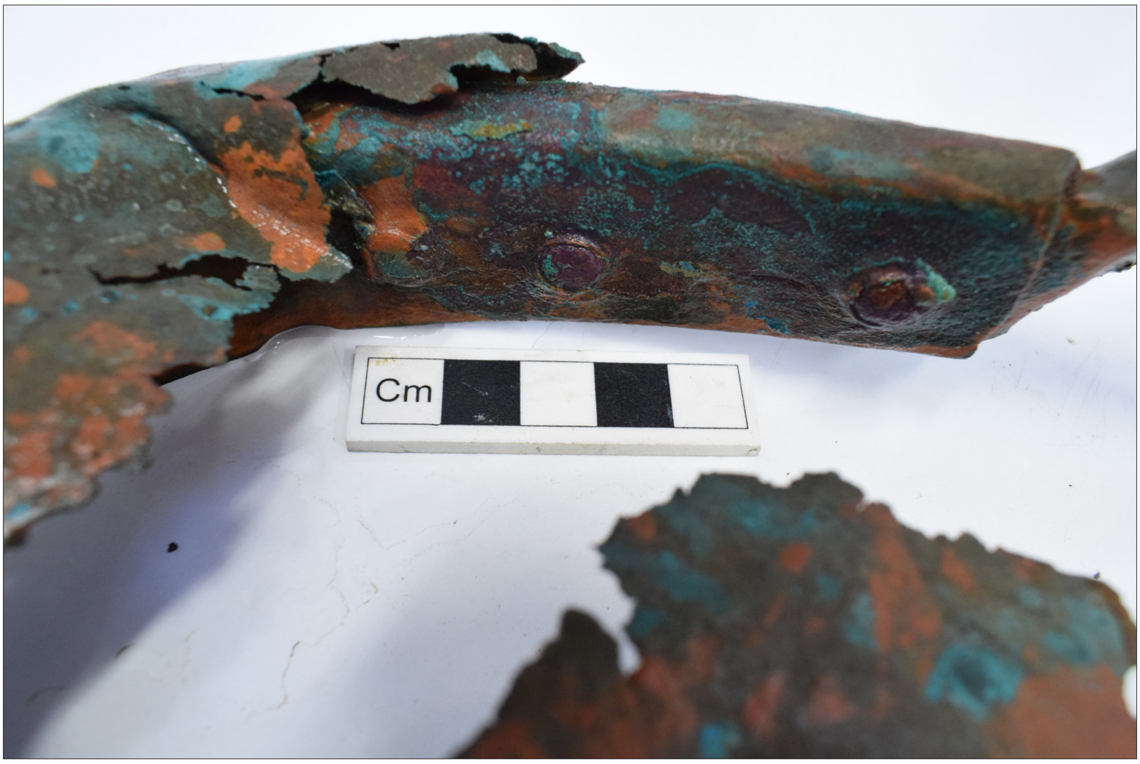

Fig 19: Object RK17 A01073 before conservation showing riveted rim.

Fig 20: Object RK17 A01073 before conservation showing riveted handle and corrosion layers obscuring mechanism.

Fig 21: Top view of obverse side of object RK17 A01073 before conservation.

Fig 22: Top view of reverse side of object RK17 A01073 before conservation.

Investigation

X-Radiography

The object was studied by X-radiography for any features that were not visible to the naked eye (Fig 23). The riveted joints on the handle could clearly be seen on the X-radiograph. Also, the X-radiographic investigation gave more insight into the fractures in the material and the stability of the object.

Fig 23: X-radiograph of object RK17 A01073 (P4472-4475, kV: 100, mA: 3, exposure time in sec.: 2).

X-Ray Fluorescence

The material composition of the pan was studied using handheld x-ray fluorescence (pXRF). As the lid consists of different elements, multiple analyses were done. In total four areas were analysed, two on the handle, one on the lid cover and one on the hoop. The results of the analyses were clear: the handle consists of approximately 97.5 wt% Cu, 1.7 wt% Pb with traces of Ni, antimony (Sb), As and Zn and is therefore of copper . The material of the lid and the strip are almost identical showing they are also copper. The measurements gave approximately 98.9 wt% Cu, 0.1 wt% Pb with traces of Ni, antimony (Sb), As and Zn.

Conservation

The object was mechanically cleaned using a scalpel and wooden skewer. Adhering sediment was found to detach easily from the object.

Only corrosion layers with adhered sediment like sand and shells were removed as these were identified as external corrosion layers and not part of the original object. This sediment was mainly located under folds in the metal and in small depressions. No new features were discovered, but the riveting mechanism was uncovered, allowing it to be visually studied (Figs 24 a-b).

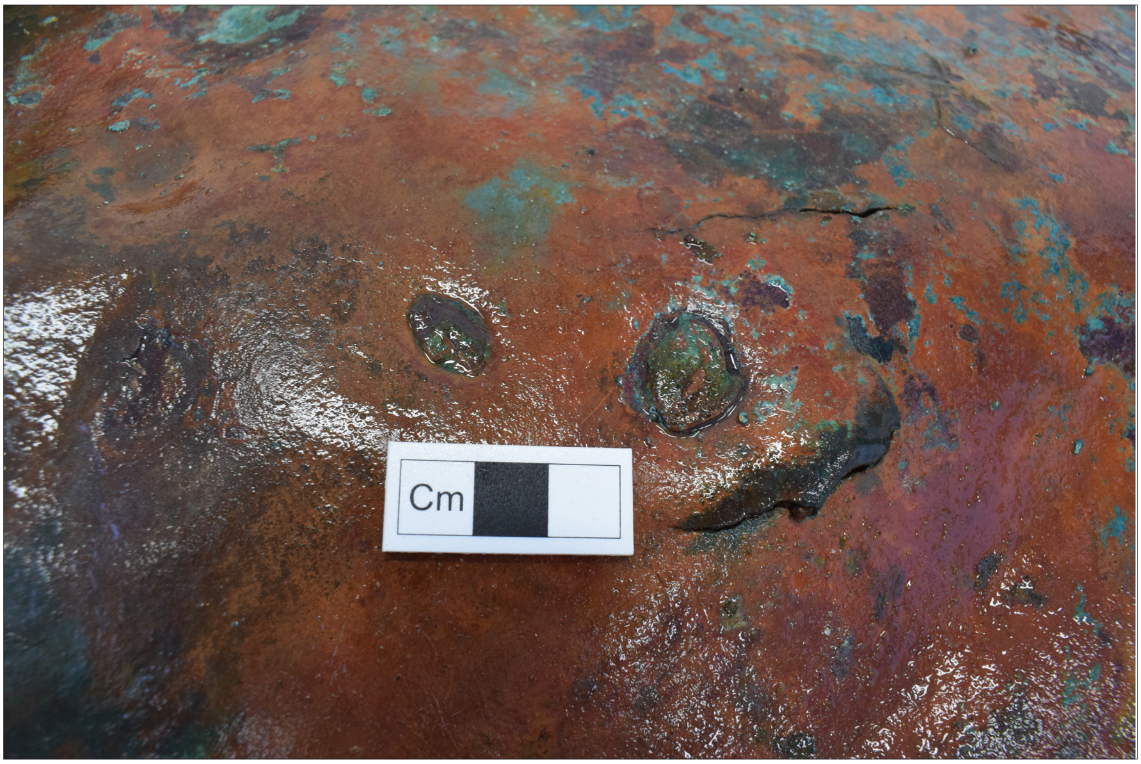

Fig 24a (top) and 24b (bottom): Object RK17 A01073 showing riveting of handle on obverse and reverse side of the lid.

CONSERVATION STATE COPPER ALLOY OBJECTS

Copper corrosion in the marine environment

Various properties of copper alloys affect the corrosion of copper in a marine context. Firstly, copper compounds are toxic to marine organisms, which greatly reduces marine growth on any surfaces (North 1987: 232). Secondly, copper and its alloys, immersed in seawater, will corrode at a rate that is dependent both on their chemical composition and microstructure, and especially the amount of dissolved oxygen in the water (Scott 2002: 67; Macleod 1994: 269). In aerobic environments corrosion layers consisting of copper oxides, copper carbonates and copper chlorides can be expected. On objects buried in sediments (and so recovered from oxygen depleted environments) copper sulphides are a common corrosion product due to activity by anaerobic sulphate-reducing bacteria (SRB). These bacteria reduce sulphate, producing hydrogen sulphide as an end product (Scott 2002: 227).

Lastly, copper alloys from a marine context often have fairly thick uniform concretions adhered to the surface which are almost entirely composed of calcium carbonate and copper(II) oxychlorides (paratacamite etc.) mixed with tin oxides (Cronyn 1990: 217). Another type of encrustation forms if iron has corroded near copper and its alloys, for they can become firmly embedded within a shell of ferrous concretion (Ibid.). This concretion crust protects the underlying copper alloy and reduces corrosion to insignificant levels.

The colours (reddish browns, greens) and composition of the superficial corrosion products on the three artefacts recovered from the Rooswijk suggests that most corrosion products conist of copper oxides, copper carbonates and copper chlorides, which would indicate an aerobic burial environment.

Both the cauldron and the lid discussed in this report are copper-zinc alloys, or brasses. Brasses are more susceptible to stress corrosion than other copper alloys. Stress corrosion occurs at sites on the object where there is physical strain in the crystal structure, resulting in stress cracking in the metal. This process is clearly visible on the cauldron.

The objects discussed in this report are in a fairly good condition. Although they are fragile and broken to a certain extent, the copper alloy itself is still reasonably intact. Most probably this state of preservation is connected to the iron corrosion that was found adhering to the surface of some of the artefacts. As discussed, the iron protected the metal underneath.

The difference in pXRF measurements on different places on the cauldron in all probability has to do with the same mechanism. The measurements taken on areas of the object where thick concretion layers were removed contained more lead and tin due to the lack of any dezincification or destannification processes having taken place. In contrast, areas where less lead or tin was recorded included the exposed areas on the external wall of the cauldron and on the rim where corrosion processes will have been more pronounced.

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