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METALLOGRAPHY OF COPPER AND ITS ALLOYS RECOVERED FROM NINETEENTH CENTURY SHIPWRECKS

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ABSTRACT

This study concerns the metallographic examination of a range of spikes and nails recovered from historic shipwrecks. The fastenings made of copper, brass and bronze were recovered from the wrecks of the *Rapid* (1811), *James Matthews* (1841) and *Eglinton* (1852). The study revealed a range of impurities and microstructures that provided good evidence for the method of fabrication. A comparison of the microstructures and the related corrosion phenomena is of interest because of the differences in the nature of the wreck sites and the origin of the vessels. The *Rapid* was an American China trader built in 1807. The *Eglinton* was English, but built in Quebec in 1842, while the *James Matthews* is believed to have been constructed in France between 1820-35 and refitted in England after her capture as the slave trader *Don Francisco*. Chemical and metallographic evidence can be used as a guide to the provenance of the fixtures on the vessel.

INTRODUCTION

Ships' fastenings based on copper and its alloys with tin and zinc are ubiquitous on wreck sites dating from nineteenth century wooden vessels. Although these objects are more readily stabilized than iron they often require a sensitive approach to their preservation (MacLeod, 1987). An archaeologist can catalogue, draw and weigh the fastenings and make notes on corrosion patterns but without further studies the story of how a vessel was built cannot be properly interpreted. The work presented in this paper is concerned with items, recovered from three wreck sites off the Western Australian coast, that have been sectioned and examined metallographically. The results are interpreted with the help of elemental analyses and microhardness measurements.

The physical environment of the wreck sites varies from the anaerobic *James Matthews* lying under several metres of sand in Cockburn Sound to fully aerobic sites. The *Rapid* sank inside an offshore reef in 8 metres of water, 1.5km from Point Cloates and the *Eglinton* lies 50km north of Fremantle in 4m of water. Apart from the differences in micro-environment, the corrosion performance of the fittings will be dependent on their composition and the stresses associated with their manufacture and ultimate function. Previous studies reported on the effects of composition (MacLeod, 1980) and microstructure (MacLeod and Pitrun, 1986) on long-term corrosion performance. The *James Matthews* is believed to have been built in France somewhere in the period 1820-35 and subsequently captured and refitted by the English (Henderson, 1980). Both the *Rapid* and the *Eglinton* were built in North America; the former at Braintree, Massachusetts in 1807 and the latter in Quebec in 1842.

For convenience, the discussion will be grouped according to the broad categories of fastenings made from copper, brass and bronze. Where the choice of description between an object being described as a brass or bronze is difficult the category has been assigned on the basis of microstructure.

EXPERIMENTAL

A total of twenty fittings were examined metallographically after they had been sectioned and embedded in Polyester casting resin, Araldite D or in Bakelite. Surfaces were prepared by grinding with wet and dry carborundum paper to 1200 grit and polishing with diamond paste to ¼-1 micron; the etchant was 2 wt% ferric chloride in ethanol. Larger objects, up to 60cm long, were sampled in six places with three longitudinal (LS) and three transverse sections (TS) representing the tail (shank), body and head regions of the spikes and nails. Where the spikes had been broken in the shipwreck itself only four sections were taken since the tail of the fitting remained on site in the hull timbers. Smaller objects such as nails, up to 15cm long, were sectioned in four ways; a longitudinal section at the tip, transverse sections in the middle of the body and under the head and a longitudinal section of the head. The sections are labelled according to the diagram illustrated in figure 1.

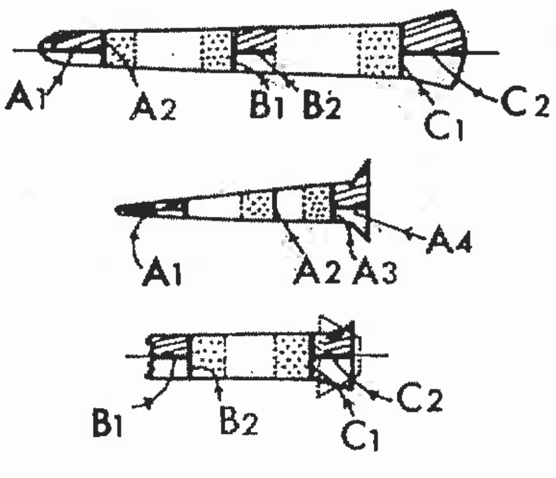

Figure 1: Sectioning diagram for ships' fastenings.

After the fittings had been examined as polished sections major differences in microstructure between the copper, brass and bronze objects were apparent. Representative samples from each type of material were taken from the different wrecks and were dissolved at room temperature in 10% nitric, 5% hydrochloric and 2% tartaric acids; this procedure avoids volatilisation of antimony. Core samples weighing 360±100mg were taken in an attempt to overcome the problems associated with sampling archaeological metals (Caley, 1964). The alloys left no insoluble residues and the elements were analysed using a Varian AA4 Spectrophotometer, except for arsenic which was determined commercially (ANALABS) by hydride generation after pretreatment with potassium iodide to remove the bulk of the copper and to reduce arsenic from the pentavalent to the trivalent state. The results of the analyses are listed in Table 1.

Vickers microhardness measurements on the polished sections were made using a Tukon Model 300 operating on a 400 gram load with a x10 objective; grain sizes were measured with the same instrument or by the ASTM method using a metallurgical microscope. Several sections were examined under the scanning electron microscope at CSIRO Division of Mineralogy (Floreat) using the back scattered electron/low vacuum mode (Robinson, 1980). Qualitative elemental analyses were done using the EDAX attached to the JSM2.

DISCUSSION: COPPER SPIKES AND NAILS - *RAPID* SPIKE 3074

Inspection of the data in table 1 shows that this spike is a leaded arsenical copper with small amounts of tin, antimony, silver and bismuth and traces of iron and zinc. The microstructure of the spike is formed with fully recrystallized grains of the primary solid solution α. Over the whole volume numerous Cu_2O and Pb-rich particles have been found. Their shape and density of distribution depend on degree of deformation; they are more elongated and closely distributed in the shank of the spike because of the higher degree of deformation at the tip compared with the body. The distortion is only seen in longitudinal sections since their shape is circular in transverse sections. There are more cuprite (Cu_2O) inclusions than microdroplets of lead.

Because there is no difference between the fully recrystallized structure and the structure obtained by cold-working followed by full annealing (Rollason, 1973) it is impossible to tell unambiguously, whether the intermediate product (Cu rod) has been hot or cold-worked. However, the spike may have been fabricated from a long rod of required thickness which had been hot or cold-worked (probably rolled) and then chopped to the right length. The grains in the shank are smaller (ASTM 25-35μm) than in the head (50μm). The spike has a squared cross-section and the grains in the head are deformed as a result of cold-hammering to get the spike into the sound oak wood. The microhardness of the A1 longitudinal section of the shank is essentially uniform over its whole length with a value of 113±5 HV. Where lower hardness is found in the A2 transverse section it is due to the presence of intergranular corrosion to a depth of 200μm. The cold hammering of the head is reflected by the hardness reaching a maximum of 137 approximately 3mm down from the head in the midline of the LS; the hardness then falls away linearly at a rate of 4.3 HV per mm to a minimum of 86 HV. A map of hardness across the maximum width of the head (LS) is uniform apart from peaks up to 134 within 200μm of the edges which fall rapidly to a mean value of 120±2. As we move down from the head of the spike towards the shank the sequential transverse sections show similar trends in microhardness, i.e. higher at the edges due to working but only to an increase of about 10% in hardness and the same average value in the centre. The 113 HV value in the shank section is probably a reflection of the smaller grains size compared with 86 HV value for the larger grains in the head in the absence of hardening from cold-working.

RAPID SPIKE 3189

The composition of the spike is typical of an arsenical copper (see table 1) that is essentially free of any other major 'impurities'.

The microstructure of the spike (3189) is basically the same as for 3074 but the Cu_2O inclusions were softer and so it was probably made in the same way though it has a round transverse section compared with the more squared sections of RP 3074. The grain size in the tail (shank) section ranged from 50-60μm which were larger than in the main body which were typically 35μm. The optical microscopy did not reveal any deformation of the head but the microhardness measurements on the C1 transverse section immediately under the head showed different behaviour to that of RP 3074 in that the hardness was seen to increase as the section was traversed. The average value of hardness at the edges of the 21mm round section was 125±5 and the variation followed a distorted 'S' curve with a minimum of 94 HV at 20% across the midline and a maximum of 160±3 HV at 80% across the diameter. This anisotropic behaviour is probably due to non-uniform heating.

The grains in the harder region were smaller than at the extremities of the section and were irregular in shape. The annealing of the shank that increased the grain size was insufficient to relieve stress associated with the initial fabrication of the spike.

JAMES MATTHEWS SPIKE 150/T6

The composition of the copper spike is very similar to those from the *Rapid* except that it has higher tin (0.41%), arsenic (0.42%) and bismuth (0.128%) impurity levels. The spike is broken in the middle of the body (see figure 1). The middle of the spike consists of fully recrystallized grains of α solid solution with a small number of Pb-rich as well as Cu_2O and Cu_2S inclusions. The microstructure of the head is much the same except that the grains are deformed with bent twins and inclusions whose orientation has been changed. Since the microstructure is essentially uniform (except for the cold deformation in the head) the spike has either been annealed after being cold-worked or it has been hot-worked. The intergranular cracks under the surface of the head and in C1 transverse section may be due to the high levels of bismuth which
lowers

the malleability of copper and will cause it to crack during extensive working (Archbutt and Prytherch, 1937). The maximum distortion in the C2 head section is found 1500μm in from the maximum width of the head (LS) where the hardness is 178 HV - the distortion rapidly falls away to a value of 117±7 for the middle of the section. At the crown of the head the maximum hardness is found 480μm into the body and it falls off at the same linear rate of 4.3 HV/mm as observed in the cold-worked C2 section of RP 3074. The fully recrystallized grains of the α solid solution in the centre of the body have a hardness of 86±3 HV with the hardness increasing to 132±2 (C1, TS) and 110±2 (B2, TS) at the edges of the circular sections. Analysis of the variation of hardness with distance from the edge in these cross-sections shows that they conform to the general equation $HV = ax^{-1} + b$, where b is the minimum hardness at the furthest distance from the edge and x the distance in microns.

JAMES MATTHEWS: NAIL 150/T13

The composition of this nail is essentially the same as for 150/T6, i.e. an arsenical copper with a small amount of lead (0.1 wt%). The complete analysis is found in table 1. The microstructure of this nail is very similar to that describing JM 150/T6 and the same type of Cu_2O, Cu_2S and Pb-rich inclusions are found. The levels of tin, arsenic and bismuth impurities (see table 1) are somewhat smaller but this does not have an obvious affect on the microstructure. The main physical difference between the two nails is the shape of the head viz JM 150/T13 has a clearly defined square head with bevelled edges whereas JM 150 has a mushroom shaped head. Some transcrystalline cracks were observed in the body close to the broken end and cold deformation is present in the C1 section under the head which was formed in the last step of the manufacturing process. As was found with the spikes from the *Rapid*, the hard working of the head increases the HV value from 86 for the fully recrystallized grains to a maximum of 146. The degree of distortion of the grains in the T6 and T13 longitudinal head sections is similar but the maximum hardness values of 178 and 146 are quite different. The differences may be due to the higher levels of tin, arsenic and bismuth found in the T6 spike.

JAMES MATTHEWS: NAIL 160/T8

The composition of this nail is essentially the same as 150/T6/T13 except that it has a much higher bismuth impurity level (0.255%). The microstructure is significantly different in that it consists of deformed grains of the α solid solution with inclusions of Cu_2O, Cu_2S and Pb-rich materials. The deformation of grains and the presence of bent twins proves that shaping took place by cold-hammering. The shank has an oblong cross-section which means that it has been squashed more from one side than the other. This effect is seen even on transverse section of this part of the nail where inclusions are squashed and distributed in lines. Further sections show that this effect is gradually lost towards the head. Under the surface laps have been found which probably resulted from improper cold-working (cold forging) of the rough surface of the intermediate "wire" form. As observed with the high bismuth content of 150/T6, this nail has transgranular corrosion cracks under the surface of the head. The effect of cold-working in the production of the nail is reflected in the microhardness which is 205±2 at the tip and along the first 8mm of the longitudinal A1 section, in the middle of the section 16mm from the tip the hardness was still high at 145±2. This value is typical of the values in the C2 section (LS) of the head. The lower average hardness in the centre of the body of the nail is 124±4 which is due to the outer layers having absorbed more of the deformation due to cold-working. The hardness at the tip may have been partly increased by the resistance experienced when it was driven into the ship's timbers.

BRASS: *RAPID* SPIKE 0000/T13

The brass spike has a high lead content (1.90%) with a small amount of tin (0.32%) as an impurity with the major alloying element of zinc at 26.39% (see table 1). Since the microstructure of this spike is markedly different along its length the three main sections will be described separately.

Head and Adjacent Body:

The microstructure is formed with cored dendrites of α primary solid solution and a tin-rich phase which is present in interdendritic regions. Pb-rich particles are placed in interdendritic regions as well, individually or in association with tin-rich phases and their shape is mostly angular and they sporadically fill shrinkage cavities. The structure and colour of the spike is typical of a 70/30 brass with a small amount of Sn. Brass normally has good resistance to corrosion, but this part of the spike is quite roughly corroded under the surface (interdendritic type of corrosion) particularly under the head. This is reflected in the microhardness measurements which have values of 105±10 in the corroded zone which extends up to 2000μm into the head along casting fault lines but is generally confined to a depth of 450±50μm. The hardness is greater closer to the surface with 160±10 HV values occurring in the first 2mm. The maximum hardness of 170 HV is associated with the tin-rich interdendritic phase; the mean hardness of the α cored dendrites is 132±4. A shrinkage cavity is in the middle of the head (approx. 1.5 x 4.2mm) which reflects poor foundry practice.

Middle Section:

This part of the spike is really very interesting, because it contains two different structures. One of them is the as-cast structure, as found in the head and the one is formed with grains of the α solid solution containing twins. This twinned structure arose from the original as-cast structure as a result of the plastic deformation. These structures are not mixed together and the twinned structure occurs close to the surface. This structure also has traces of cold-working, i.e., grains are deformed and they contain bent twins. A plot of the microhardness of the section shows a linear response to the deformation in that HV values increase from the α dendritic value 136 to a maximum value of 230 at a distance of 1000μm from the edge of the section and fall to 144 at 2700μm relative to the same position. Hardness values on the side of the section away from the deformation increase to a maximum of 177 associated with the tin-rich interdendritic phase only 250μm from the surface.

Tip Section:

Moving towards the point of the shank the grains lose coring typical of the as-cast structure and the microstructure is formed with fully annealed grains of a α solid solution. The Pb-rich particles have circular shape. There is extensive intergranular corrosion along the edges of the longitudinal section. The tip has some very heavily deformed grains (139 x 23μm) and a hardness of 274 which falls rapidly to the fully annealed value of 113±1.0 HV. The manufacture of the spike was via an initial casting (see head microstructure) followed by a small degree of cold-working (probably cold-hammered) that caused the two different structures in the main body. The end of the spike was annealed and the distortion and hardening of the tip would have resulted from the nail being driven into timber. In the centre section a large hole was found which was probably due to a casting pipe. Sea water penetrated this area and the major corrosion product identified was $Sn_4(OH)_6Cl_2$. The low level of arsenic impurity in the spike was insufficient to prevent significant corrosion of the brass.

EGLINTON: NAIL 1379/T2

The composition of this brass nail is very similar to that used in the *Rapid* with the main difference being an extra 4.2% zinc in this sample. Although the *Eglinton* was built in Quebec in 1842 and the *Rapid* near Boston in 1807 the similarities of the trace levels in iron, silver and nickel (see table 1) are indicative of a common source of materials. The microstructure is typical for a cast α brass (cored dendrites of α solid solution) which contains a little bit of β phase in the interdendritic areas. In these areas Pb-rich particles are also found. The presence of "hot tear" fractures is probably due to premature removal of the nail from the mould when the β phase had not fully solidified. It is possible that the tear lines were not as deep as they currently appear (up to 60% of the cross-section) but that the initial defect has been exacerbated by 125 years of corrosion. The crack has undergone extensive dezincification of the zinc-rich β phase. The normally beneficial effect of arsenic on dezincification has probably been masked by the relatively high level of iron (0.165%) as an impurity (Oishi, et. al., 1982). Microhardness measurements on this brass nail showed marked differences to that observed in the RP 0000/T13 spike. The longitudinal section of the nail showed a linear increase in hardness from 94 at the tip to a steady value of 134 as found in the *Rapid* spike. This change is largely due to the gradual change from columnar grains (104 x 19μm) to equi-axed grains (30 x 30μm) in the centre of the section some 12mm from the tip. Similar behaviour was observed with the transverse section through the middle of the nail except that the linear slope was 21 HV mm^{-1} compared with 3.7 HV mm^{-1} for the tail section and the hardness ranged from 141 to 182 HV.

BRONZE: *RAPID* NAIL 3373A

The composition of this mixed tin/zinc alloy with copper is shown in table 1 and is like a heavily leaded bronze in its appearance. The nail is in its as-cast condition and was found in the area of the wreck associated with the ship's stores and it has not been mechanically worked or heat treated. The microstructure has cast character and is based on cored dendrites of primary α solid solution. In the as-polished state the lead is visible as fine dark particles in the interdendritic positions. Using higher magnification the interdendritic areas also have small amounts of α plus δ eutectoid (δ - $Cu_{31}Sn_8$) as minute light islands and grey sulphide (of zinc or lead) inclusions which are individually present and in association with lead. In the whole volume of the nail a lot of shrinkage porosity has been detected. The macro-structure has typical characteristics of bronze castings and it is formed with relatively big columnar grains and with a few equi-axed grains in the centre of the nail. Microhardness measurements on the four sections showed minimum readings of 84 HV on a large α dendrite with mean values of 93±1 for the longitudinal section of the head going down the midline towards the tip. The hardness within the first 200μm of the surfaces was typically 175±3 and was due to a high concentration of the tin-rich (α + δ) eutectoid - the concentration of tin near the surface in cast bronzes is called 'tin sweat'.

RAPID: NAIL 3373B

This leaded zinc bronze contains almost twice as much tin as 3373A (see table 1) and 1.34% more zinc. The microstructure is similar to that of 3373A, but the structure contains many more light islands of α plus δ eutectoid (circular or angular shape). Over the whole nail we can see rough gas porosity, and shrinkage porosity, which has been caused by imperfect casting technology. The equi-axed zone in this case is wider than found in RP 3373A and the grains are smaller. Under raking light tin-rich areas have been found in the interdendritic regions. The sample also shows signs of 'tin sweat'. Microhardness measurements on the longitudinal tail section give a mean value of 115±2.5 HV away from the tin-rich layer near the edges where the hardness values 178±6 extended further into the body of the nail than with RP 3373A. The hardness of the longitudinal head section showed a typical $^1/x$ dependence on the distance from the edge of the section.

RAPID: NAIL 5004/T11

This nail has an even higher concentration of tin (7.46%) than the preceeding samples from the same wreck but zinc is present only at trace levels (0.024%). The nail exists in its as-cast state and has not been mechnically worked or heat treated. Etching in 2% alcoholic ferric chloride reveals the dendritic cast structure. The microstructure is formed with cored dendrites of α solid solution with particles of α plus δ eutectoid. Lead-rich particles and sulphides occur sporadically in interdentritic areas. A lot of shrinkage and gas porosity have been found in the whole volume of the nail, which is proof again of imperfect foundry practice. Under the whole surface there are large amounts of tin-rich areas which were formed as a result of 'tin sweat'.

The microhardness values of 184±4 HV in the 'tin sweat areas are normal with a mean value of 138±7 HV for the transverse sections which is harder than in the lower tin bronzes. The main effect of the greater tin content is to increase the 'hard' zone around the edges from 200μm up to 1400μm in places.

RAPID: NAIL 3324

Although no quantitative analyses were carried out on this sample (38mm long) qualitative analysis by SEM shows it to be very similar to 3373A. The macrostructure is formed with only equi-axed grains which are a bit smaller in the shank than in the head. This macrostructure typifies sand casting and it is the only example of this type production found on the wreck. By way of contrast, the hardness <u>decreased</u> linearly from the tip as we moved down the midline towards the head and the grains became larger (a decrease from 120 to 89 HV over eleven millimetres). All the other bronze nails exhibited the reverse trend in hardness. The mean values of hardness for the larger grained head section were the same as for the 3373A sample of the same composition.

JAMES MATTHEWS: NAIL 610/T1

The composition of this small bronze nail is most unusual in that although copper accounts for 90.74% of the weight, the tin content is only 3.60%. Apart from being a medium leaded bronze the object is very unusual in that it also contains 0.84% bismuth, 1.396% arsenic and 2.32% nickel! (see table 1). The 25mm nail has been cast (as-cast structure), without any other mechanical operations. Macrostructure is formed with a columnar zone and a couple of equi-axed relatively big grains in the centre of the nail. Microstructure is typical of bronzes containing higher amounts of tin (more than 10% Sn). Microstructure has cored dendrites of primary α solid solution and a lot of islands of α plus δ eutectoid, which are placed in interdendritic areas. Pb-rich particles are present as well and also sulphides (Zn or Pb), but just sporadically. In whole nail a lot of shrinkage cavities have been found, except in the shank which is quite clear. Under whole surface tin sweat is present. It would appear that the presence of the nickel, arsenic and bismuth has dramatically changed the microstructure from that expected on the basis of the tin content. Microhardness measurements showed that the HV value in the shank fell in a hyperbolic fashion ($1/x$) with a plot of hardness vs the inverse of the distance from the edge giving a straight line (correlation coefficient 0.9973) that gave a minimum theoretical values of 153 cf. the observed value of 164. The extreme hardness observed at the tin-rich edge of the nail had values of 340! Because of the high solubility of nickel in copper the 2.32% nickel would be dissolved in the α(Cu,Ni) phase. It is likely that the high bismuth, arsenic and nickel impurities came from a copper sulphide ore body that also contained minerals such as Parkerite ($Ni_3Bi_2S_2$) and Gersdorffite (NiAsS). Since silver sulphides are also found in association with these minerals it is not surprising that JM 610 has the highest silver content, 0.235 wt%, of the fifty copper alloys analysed in these laboratories. Copper used in the manufacture of this nail appears to have come from a different source.

TABLE 1: Composition of ships' fastenings

	Reg. No.	Cu	Sn	Zn	Pb	Sb	Ni	Ag	Fe	As	Bi
COPPER											
Rapid - spike	3074	98.14	0.0375	0.0022	0.163	0.024	0.018	0.088	0.003	0.21	0.047
Rapid - spike	3189	99.41	0.050	0.0018	0.0095	0.007	0.017	0.056	0.004	0.31	0.019
James Matthews - spike	150/T6	98.60	0.41	0.0033	0.0097	0.022	0.050	0.078	0.002	0.42	0.128
James Matthews - nail	150/T13	98.38	0.049	0.0037	0.101	0.027	0.021	0.108	0.002	0.34	0.077
James Matthews - nail	160/T8	98.63	0.074	0.0025	0.109	0.009	0.047	0.104	0.002	0.29	0.255
BRASS											
Rapid - spike	0000/T13	70.04	0.32	26.39	1.90	0.049	0.074	0.078	0.165	0.022	0.014
Eglinton - nail	1379/T2	68.54	0.29	30.61	0.61	0.008	0.058	0.059	0.165	0.068	0.082
BRONZE											
Rapid - nail	3373A	89.12	2.90	3.46	3.98	0.086	0.046	0.107	0.108	0.013	0.081
Rapid - nail	3373B	84.43	5.53	4.80	3.76	0.141	0.064	0.111	0.244	0.29	0.025
Rapid - nail	5004/T11	90.3	7.46	0.024	0.81	0.545	0.086	0.151	0.056	0.042	0.231
James Matthews - nail	610	90.74	3.60	0.044	0.55	0.135	2.32	0.235	0.039	1.39	0.84

REFERENCES

Archbutt, S.L., and Prytherch, W.E., 1937 "Bismuth-arsenic-antimony-nickel-oxygen". Chapter 8 from 'Effects of impurities in copper', Res. Monograph 4, British Non-Ferrous Metals Res. Assn., London, 96-109.

Caley, E.R., 1964 "The heterogeneity of ancient metals and the sampling problem", in 'Analysis of Ancient Metals', Pergamon Press, London, p1-15.

Henderson, G.J., 1980 "Unfinished Voyages". University of Western Australia Press, p182-184.

MacLeod, I.D. and North, N.A., 1980 "350 years of marine corrosion in Western Australia". Corrosion Australasia, 5:11-15.

MacLeod, I.D. and Pitrun, M., 1986 "The effects of microstructure on long-term corrosion". Synposium 11, Lead paper, Proceedings of Conference 26 Adelaide, November. Australasian Corrosion Association, Vol. II.

MacLeod, I.D., 1987 "Conservation of corroded copper alloys: comparison of new and traditional methods for removing chloride ions". Studies in Conservation, 32:25-40.

MacLeod, I.D., 1987 "Secondhand metal - conservation and industrial archaeology of shipwreck artefacts", in 'Archaeometry: further Australasian Studies'. Ambrose, W.R. and Mummery, J.M.J., eds. ANU Press, Canberra, p280-291.

Oishi, K., Tsuji, T. and Watanabe, Y., 1982 "Behaviour of various elements in dezincification layer examined by means of X-ray micro-analyser (XMA)", Proc. Int. Symp. Corros. 'Copper and Copper Alloys in Buildings', JCDA, Tokyo, p256-269.

Robinson, B.W., 1980 "The backscattered-electron/low vacuum SEM technique: a user's evaluation". Micron, 11:333-334.

Rollason, E.C., 1973 "Metallurgy for Engineers", Edward Arnold Ltd., 4th Edn., p127.

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