Corrosion and Conservation of Tin and Pewter from Sea Water

I.D. MacLeod* and R. Wozniak

Department of Materials Conservation, Western Australian Museum,
Cliff Street, Fremantle, Western Australia 6160.

Abstract

The corrosion behaviour of a series of synthetic tin alloys with lead and antimony was studied in aerobic and anaerobic sea water over a period of one year using electrochemical techniques, electron microscopy and X-ray diffraction to determine the deterioration processes. The chemical composition of the alloys was chosen to replicate known artefact analyses and also to see the effects of the changing amounts of lead and antimony on the microstructure and the subsequent electrochemical characteristics of the materials. Simulation of crevice corrosion cells produced massive changes in the pH of the micro-environment and successfully reproduced the micromorphology and the mineralogy of many of the tin corrosion products found in historic shipwreck artefacts dating back to the 17th century. The nature of the corrosion products has been correlated with the various rates of desalination of degraded pewter recovered from historic shipwrecks.

Keywords

Tin, pewter, corrosion, conservation, sea water.

Introduction

The successful treatment of corroded pewter and tin artefacts recovered from historic shipwrecks is made more difficult because of the kinetic inertness of the tin corrosion products and the relatively poor level of understanding of the nature of the overall processes that have caused the degradation. One of the great difficulties facing workers in this field is the relatively low abundance of pewter and tin materials on the shipwrecks[1]. This means that curators are not well disposed to destructive testing of the artefacts. However, following the collapse of some corroded pewter vessels from the wreck of the Dutch Eastindiaman *Vergulde Draeck* (1656) it was possible to examine them under the scanning electron microscope (SEM). The images showed that the pustules, which characterise the worst degradation problems of aerobically corroded pewter, were only partly filled with a mass of tin corrosion products – the rest of the space was air. This is a characteristic of minerals which have formed from a gelatinous precipitate which subsequently crystallises. It became clear that an understanding of the nature of the original condition was essential to help us in the search for a successful conservation treatment. Since access to pewter artefacts on the shipwreck sites was not possible, because of their small size and unknown location, we could not perform the normal range of *in situ* measurements of corrosion potentials (E_{corr}) and surface pH that have been so informative

about the nature of corrosion on iron and copper alloys on historic shipwrecks[2–5].

It was decided to examine a series of synthetic alloys to overcome this problem. Previous work has shown that electrochemical methods of studying the corrosion of historic metals can provide very useful information on why sections of the same object can corrode in a markedly different fashion[6–8]. The tin synthetic alloys containing antimony were standard Britannia metal and a low tin-lead seam solder found on a lead scupper on the wreck of the French built vessel the *Lively* (1820), which was wrecked on the Rowley Shoals off the coast of Western Australia. A further five synthetic alloys of tin and lead completed the range of compositions (Table 1). Several samples of each composition were poured at the same time to ensure that the materials used for metallographic analysis and for corrosion experiments were as similar as possible.

Table 1. SEM/EDXRA analysis of synthetic tin and lead alloys (wt %)

Metal	Tin	Lead	Antimony	Copper
Tin	100	–	–	–
Britannia	91	0	7	2
75Sn/25Pb	75	25	–	–
Eutectic	61.9	38.1	–	–
Seam solder	28.4	68.2	3.2	0.2
25Sn/75Pb	25	75	–	–
Lead	–	100	–	–

*Author to whom correspondence should be addressed

Experimental Method

The synthetic alloys were prepared from pure metals (99.9 wt % purity) and were weighed out according to the required composition. The metals were melted by direct application of a flame from an oxy-acetylene torch. Any surface dross was physically removed from the molten metals before casting commenced. Each batch of molten metal was poured from a clean crucible into a steel mould. The mould consisted of a series of a dozen 12 mm diameter holes in a solid 120 mm diameter steel block. After being removed from the mould the samples were either sectioned and polished for metallographic analysis or were connected to insulated copper wires by soldering the rear face of the cylinder and then mounted in a polyester resin to use as electrodes. The mounted samples were prepared for by polishing with wet and dry carborundum papers to 1200 grit and then with diamond to 1/4 micron. Microhardness measurements were made using a Tukon Model 300 microhardness machine using a 200 gram load with a x20 objective. Electrochemical corrosion measurements were made at the Chemistry Centre (WA) using a Versastat EG&G Princeton Applied Research instrument at scan rates of 0.5 mV/sec on samples which were scanned ±250 mV from the open circuit voltage, measured against a saturated calomel electrode. Measurements on freshly immersed synthetic alloy electrodes did not give reproducible results so the electrodes were aged in natural sea water for several weeks before further measurements were made. This greatly improved the stability and reproducibility of the data. The scans were repeated up to ten times until reproducible results were obtained. Great care had to be taken with polishing the soft synthetic alloys to prevent surface contamination.

The crevice corrosion experiments were performed over periods of between four and seven months. The two electrode faces were kept separated by 0.5 mm sections of nylon fishing line on either side of the centrally located metal section. The nylon line was fixed to the edges of the polyester resin blocks by spots of acrylic cement and the whole assembly was held together by elastic bands. This arrangement greatly assisted access for subsequent chloride and pH measurements on the corroded surfaces. One of the electrodes in each pair was electrically connected to a 50 cm^2 copper plate which was separated from the test cells by a salt bridge. This arrangement accelerated the corrosion process in the crevice cells through galvanic coupling. After immersion in sea water of 35% salinity(0.56 M chloride) the E_{corr} values, relative to Ag/AgCl, were recorded manually by reading the digital voltmeter. At the end of the experiments the surface pH readings were made using an Activon flat bulb combined glass electrode and the chloride ions were measured with a calibrated Orion chloride ion electrode. Anaerobic conditions were simulated by adding 5×10^{-3} M sodium sulphide to sea water which was deoxygenated with argon. A low oxygen environment was maintained by a blanket of liquid paraffin oil over the solution. The SEM examinations were done with either a Jeol JSM2 instrument with an environmental cell or a standard Cambridge Stereoscan 360 with a Link EXL-10 x-ray analysis instrument.
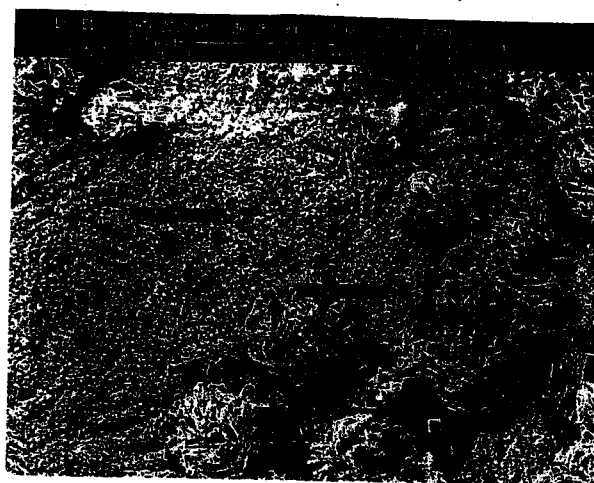

Figure 1. SEM micrograph of the secondary image of a pitted Britannia metal coupon showing $SnCl_2$ and SnO_2 crystals – image width 380 μm

Results and Discussions

The identification of the corrosion products from historic shipwrecks can often provide a useful insight into the nature of the conditions of burial of the artefacts[9,10] since Pourbaix diagrams can tell the range of E_h and pH under which the various minerals are stable. Previous work[11] has reported that the tin corrosion products found on pewter artefacts are dominated by cassiterite [SnO_2] with other tin(IV) species such as schoenfliesite [$MgSn(OH)_6$] being relatively rare. The divalent tin corrosion products $Sn_4(OH)_6Cl_2$ and hydroromarchite [$Sn_3O_2(OH)_2$] are all indicators of the fact that once the initial oxidation of tin has taken place to produce Sn^{2+} ions the metal ions and complexes will be hydrolysed to form mixed oxides or chloride/hydroxides. Concomitant oxidation and hydrolysis also produces a range of tin(IV) compounds, most of which have X-ray diffraction patterns that do not match any of the compounds listed in the JCPDS index. This is consistent with them having grown from a primary gelatinous precipitate.

In the crevice corrosion experiments the major phase found on the surface of the Britannia metal was $SnCl_2$ with traces of blue copper corrosion products and some $MgSO_4$ – (Figure 1). The morphology of this and other deposits containing schoenfliesite and abhurite [$Sn_3OCl_2(OH)_2$] was very similar to one of the dominant tin minerals found in pustules. An example from a pewter spoon from the *Zeewijk* (1727) is shown in Figure 2. The cotunnite [$PbCl_2$] crystals found on the surface of the pitted 75Sn/25Pb coupons was identical to those on the *Zeewijk* spoon. Other tin hydroxy chlorides found on the surface of 75Sn/25Pb coupons exposed to open sea water included the tin(II) compound $Sn_{21}Cl_{16}(OH)_{14}O_6$. The corrosion products on the 25Sn/75Pb coupons were dominated by hydrocerussite [$Pb_3(CO_3)_2(OH)_2$] with some laurionite [$Pb(OH)Cl$]. Other chloride containing species found on lead artefacts include penfieldite [$Pb_2Cl_3(OH)$] and phosgenite [$Pb_2(CO_3)Cl_2$]. When the metal coupons were separated after four months in sea water, the surface pH of the coupons had fallen considerably from the initial pH value (8.12) of the crevice and the chloride concentra-

Figure 2. Backscattered SEM micrograph of a *Zeewijk* pewter spoon showing honeycomb SnO_2 and $Sn_4(OH)_6Cl_2$ – image width 220 µm

Figure 4. Pourbaix diagram for the Sn/H_2O-Cl system at 298K, with a dissolved tin activity $=10^{-6}$, $a_{Cl^-}=2.5$; the hatched area covers the range of conditions observed in the crevice corrosion cells

tion had also significantly increased. The most acidic pH was associated with the pitted surfaces of the metals which had been electrically connected to a corroding copper plate in an adjacent reaction vessel. The 100% tin and the Britannia metal had a mean pH of 4.0±0.1 in the crevice and the amount of chloride was at least 1.6 M, which is almost three times as concentrated as the surrounding sea water (Figure 3). In a closed corrosion cell there is a concomitant increase in chloride concentration as the pH decreases. The highest chloride concentration observed was 2.5 M, or more than 4½ times that of the sea water.

The high acidity and high chlorinity associated with the crevice corrosion experiment is consistent with the presence of the corrosion products observed on the experimental and artefact surfaces. The Pourbaix diagram for the Sn/H_2O-Cl system[12] shows that the tin(II) hydroxychlorides dominate the region of the E_h-pH diagram associated with the moderate acid, low oxygen and high chloride environment of the pits (Figure 4). The ability of tin(II) chloride complexes to form and diffuse through fissures and defects in any passivating film is clearly a major factor in determining the ultimate fate of the artefacts *in situ* and in humid storage environments. The distribution diagram of the Sn(II)-

Cl system[12] shows that at a chloride concentration of 2.5 M the $SnCl_4^{2-}$ and the $SnCl_x$ ions each account for 40% of the soluble tin species. Inspection of sectioned pewter artefacts provides evidence of the outward movement of tin complexes through defects in a surface patina. This is clearly seen in the section of a tin-antimony pewter artefact from the *Rapid* (1811) in Figure 5. The dark grey phase is a copper-iron-sulphide $CuFeS_x$ which seems to have formed after the object was buried in the sediments on the bottom of the sea. Tin corrosion products have diffused through the cracks and have been precipitated on top of the original surface.

The artefacts on the *Rapid* wreck site have been shown to be subject to periodic exposure and re-burial[10] in the sediments. For pewter artefacts, the tin(II) chlorides produced in the primary corrosion reaction are hydrolysed, oxidised and precipitated as either tin(II) or tin(IV) species, as they interact with the less acidic and lower chloride environment of normal sea water. The competition between the rates of oxidation and hydrolysis is reflected in the presence of several mixed
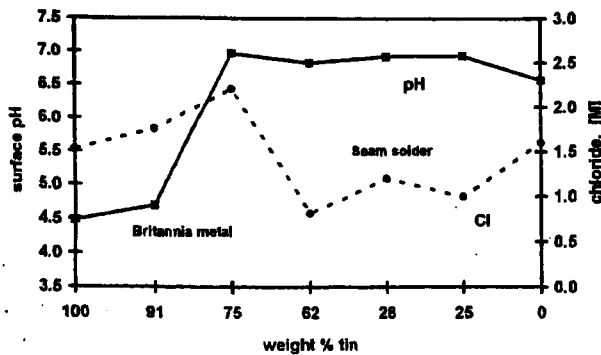

Figure 3. Surface pH and chloride concentration for crevice corrosion cells, after seven months in sea water, as a function of the composition. The compositions of the alloys are listed in Table 1
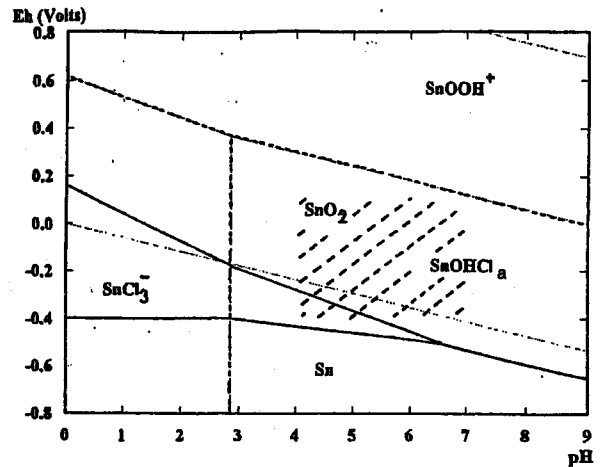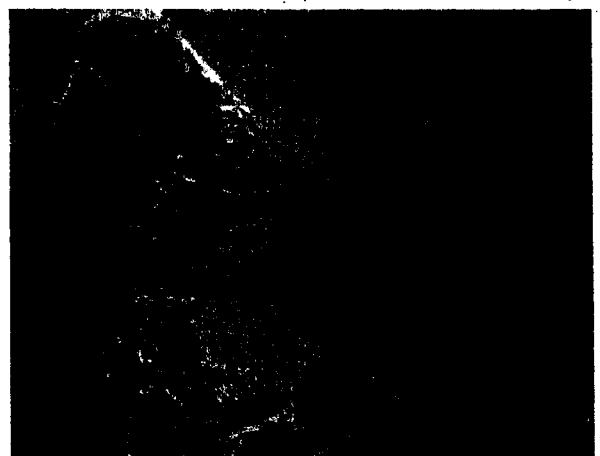

Figure 5. Backscattered secondary SEM micrograph of a corroded Sn/Sb pewter from the *Rapid*. The left of the image is the seaward surface, the dark phase is a copper-iron-sulphide. Image width 200 µm

Figure 6. Backscattered secondary SEM micrograph of the *Rapid* pewter Sn/Sb pustule. The roseate phase in the upper right corner is the residual intermetallic SnSb phase. Image width 260 μm

Sn(II)/Sn(IV) species in pewter corrosion products[11]. Further into the metal the residual intermetallic SnSb phase is seen as the roseate crystals while the bulk of the material consists of copper corrosion products (light grey spots) in amongst a tin-rich grey matrix, as shown in Figure 6. Similar selective corrosion of tin and copper was observed in the Britannia metal coupons. It is probable that the pustules formed on the surfaces of the pitted Britannia metal and pewter artefacts are largely caused by internal pressures associated with crevice corrosion. The combination of the increased volume of corrosion products in the crevices and the very soft nature of the alloys results in pustule formation. The microhardness measurements (Vickers scale) of the synthetic alloys confirms the soft nature of the tin-lead synthetic alloys, as seen in Table 2.

Sectioned pewter pustules from artefacts show that the upper surface of the pustule typically contains residual metallic phases. The worst examples of blistered "pewters" are associated with antimony-tin compositions similar to Britannia metal. Surface marks associated with the manufacture of the artefacts are sometimes retained on the surface of the corrosion blisters. Addition of antimony is known to increase the hardness of tin lead synthetic alloys in a linear fashion[13]. This is apparently sufficient in many cases to allow the surface to remain intact while it is undergoing major distortion due to the pitting corrosion reactions underneath the surface. Even with the addition of antimony the synthetic Britannia metal is only two times harder than the binary tin-lead alloys. The surface of the synthetic Britannia metal alloy showed the same pustular formation as observed on *Vergulde Draeck* pewters after only six months in the crevice corrosion cell. The combination of the formation of intermetallic Sn/Sb phases, the selective corrosion of

tin, and the softness of the metal results in the formation of the characteristic pustules.

Initial and Long Term Corrosion Rates

Inspection of the current voltage curves from the electrochemical experiments with the coupons in normal aerated sea water showed that in the absence of pitting phenomena, the apparent corrosion rate fell by a factor between 9–15 times as the coupons aged in sea water over a period of four months. The drop in corrosion rates is to be expected with the formation of protective passivating films over the surfaces of the synthetic alloys. Where pitting took place the corrosion rates could increase by as much as 500 times compared with the overall corrosion rate. After two months of exposure to anaerobic sea water containing approximately 5×10^{-3} M sulphide ions, simulating significant biological activity, the corrosion rates of the coupons were five times less than the equivalent rate in aerobic sea water. This is consistent with observations on historic shipwreck pewter artefacts recovered from anaerobic and aerobic micro-environments. Long term anaerobic corrosion rates were calculated to be of the order 0.0074 ± 0.0023 mm/year, which equate to a depth of 2.4 ± 0.7 mm for pewter from the *Vergulde Draeck* and 1.3 ± 0.4 mm for material from the *Lively* if it had been in an anaerobic micro-environment on the site. The calculated corrosion rates are consistent with observed values of corrosion on material recovered from anaerobic concretions where the objects have protective patinas of complex minerals such as stannite $[Cu_2FeSnS_4]$.

Apart from the normal range of corrosion products found in aerobic sea water, the metal samples exposed to "anaerobic" conditions formed galena [PbS] on the range of binary Sn/Pb coupons and on pure lead. The antimony mineral klebelsbergite $[Sb_4O_4SO_4(OH)_2]$ was formed on the Britannia metal along with an unidentified phase containing tin, magnesium and sulphur. The higher electrochemical aerobic degradation rates also explain why many shipwreck pewters are totally mineralised in comparison with pewters buried in anaerobic conditions.

The passivation peak voltages (E_{peak}) show a general trend towards more cathodic voltages with an increasing amount of lead in the synthetic alloy. The peak potentials closely match the half cell potentials associated with the formation of solid phases. The 100% tin synthetic alloy which had a layer of SnO_2 on the surface had an E_{peak} -0.110(NHE), which is the same as the $E_{1/2}$ for the SnO_2/Sn potential of -0.106 (NHE). For the synthetic 25Sn/75Pb alloy coupons the formation of $PbCl_2$ was seen in the SEM/EDXRA analysis as a dominant corrosion product. In this case the passivation peak voltage was -0.286(NHE) and the $E_{1/2}$ for the $PbCl_2/Pb$ couple was -0.280 volts vs. NHE, under our experimental conditions. The trend in passivation potentials is largely dominated by the underlying reac-

Table 2. Microhardness (HV) of tin and associated synthetic alloy

Section	100% Sn	Britannia	75%Sn/25%Pb	Eutectic	Seam solder	25%Sn/75%Pb	100%Pb
Longitudinal	10.3±0.5	31.4±3.2	17.6±0.9	15.7±1.6	14.1±1.1	12.4±3.9	7.1±0.9
Transverse	10.3±1.7	27.7±3.2	18.0±1.6	19.6±2.0	15.0±0.6	14.6±0.6	6.8±0.8

tivity of the constituent elements. A comparison of the E_{corr} and E_{peak} data for the aged samples showed that, when the E_{corr} values were more anodic than the E_{peak}, the corrosion rate had decreased significantly from the initial scans. This reflects the passivating nature of the corrosion products formed on the surface of the synthetic alloy. For the 100Sn, 75Sn/25Pb the E_{corr} values were more cathodic than the E_{peak} and the corrosion rates had increased. Significant pitting was noted for these samples. Corrosion reactions increase surface roughness considerably and make comparisons of rates very difficult since we cannot assume a constant effective surface area or at least similar degrees of roughness. Optical micrographs confirm the fact that, even over the area of $1.1cm^2$, there can be a wide range of corrosion activity that results in very different surface morphologies and roughness. This is entirely consistent with the variable nature of the surface of many pewter artefacts.

The addition of other alloying elements such as antimony modifies the corrosion process at the electrode in a number of ways. The formation of the intermetallic phases with tin renders the antimony-tin pewters very prone to selective corrosion of the tin-rich phases because of the relatively inert nature of the intermetallic phase. The addition of 7% antimony and 2% copper to tin to form synthetic Britannia metal changes the relative order of what is the apparent rate controlling step. For 100% tin the Tafel slope for oxygen reduction appears to be rate controlling, while the synthetic Britannia metal has the anodic oxidation of metal being the controlling step. For the 75Sn/25Pb, the eutectic, the seam solder and 100Pb samples the reduction of oxygen is the rate controlling step. For pure tin and lead, when coupled to the full range of tin-lead alloys in nitrate media, the maximum potential difference between the phases was only 10 mV[14]. Although the differences in voltage between the phases will be greater in sea water, the basic similarity in electrochemical behaviour of the tin and lead phases makes binary tin-lead pewters less prone to selective corrosion. When selective localised corrosion occurs under the surface of the metal, the pressure on the oxidation products can cause the soft metal surface to deform and build up the characteristic pewter pustules.

Metallographic analysis of the synthetic alloys clearly indicates that the eutectic composition is less prone to localised corrosion than the alloys that are closer to either of the pure lead or the pure tin. The addition of tin to lead initially increases the electrochemically determined corrosion rate and then it falls away as the eutectic composition is approached. Because of the different corrosion characteristics of tin and lead in sea water, the addition of a small amount of an alloying constituent has a much greater effect than would be expected on the basis of the weight of the metal. More experimental work is needed on the aged samples to correlate gross physical corrosion behaviour with the composition of the microstructural phases.

Dechloridation and Conservation

Analysis of the amount of chloride removed from corroded lead artefacts shows that, for ten batches of lead objects, of similar ratios of mass to surface area,

the mean value is 1.22 ± 0.72 wt% chloride extracted during the washing programs, which ranged from simple desalination in deionised water to alkaline dithionite. Comparative data for pewter artefacts apparently falls into two categories of 1.5 ± 0.6 wt% and 5.6 ± 2.3 wt% chloride removed during treatment[15]. The data sets were chosen on the basis that they had similar surface area to volume ratios. Monitoring of the wash solutions was maintained until there was no further release of chloride ions. Treatment times ranged from a few months to two years. Soft water corrosion of lead in deionised water was inhibited by the addition of 500 ppm sulphate. Some of the washing periods examined covered periods of up to two years in deionised water to ensure complete removal of soluble chloride ions to minimise the possibilities of continued corrosion. The lower amounts of extractable chloride in pewters generally correspond to the pewters with a lead content $75\pm10\%$("lead-rich"), while the $85\pm15\%$("tin-rich") tin pewters have a much greater amount of chloride containing tin corrosion products to be extracted[15].

The presence of any "sea salts" such as $MgCl_2$, NaCl, KCl etc. on the surface of pewter artefacts is readily noticed because the desalination plots are very different to the normal simple diffusion controlled model. The "contaminated" artefacts show an initial rapid release rate which falls away, within a few days, to a steady but lower release rate. In all stages of the treatment the plots of chloride concentration against the square root of time are linear. During the initial rapid release the ratio of Na/K is close to the value of 27.8 found in normal sea water[16]. After the "sea salts" have been removed there is essentially no further increase in the sodium and potassium concentrations in the wash solutions. The amount of chlorides extracted from metal corrosion products is the difference between the total chloride and that associated with any "sea salt" contamination. In a typical washing program $68.5\pm8.7\%$ of the chlorides are removed in the first wash and $31.7\pm8.3\%$ in the second wash.

During the desalination of a series of pewter bottle tops from the wreck of the Zuytdorp (1712) the wash solutions were monitored for more than a year for tin, antimony, copper, lead and chloride ions. In some cases surface lead corrosion products were dissolved in the distilled water within two days, but the more typical response of the artefacts was that after a period of between two and three weeks the tin and lead ions would reach a maximum concentration of 5 ppm and then fall off as the ions were hydrolysed/precipitated. There was no antimony (<0.1 ppm) detected in any of the wash solutions. In essence, there was minimal mobilisation of the metal ions into the wash solutions. Comparison of the amounts of chloride extracted from corroded artefacts of similar geometry but from different wreck sites can be made by dividing the weight per cent chloride by the years of immersion in the sea water. The mean amount of chloride extracted from the "tin-rich" pewters was 0.020 ± 0.010 wt% per year and the "lead-rich" artefacts released the equivalent of 0.0041 ± 0.0017 wt% per year. When the same approach is taken with lead objects they gave 0.0038 ± 0.0019 wt% per year which is the same as for the "lead-rich" pewters. This result simply demonstrates that, for the

latter category of artefacts, the corrosion is dominated by the electrochemistry of lead. One reason for the lower amount of chloride from lead objects is that anglesite [PbSO$_4$] is a major oxidation product on lead and "lead-rich" pewters. The other dominant corrosion products are hydrocerussite [Pb$_3$(CO$_3$)$_2$(OH)$_2$] and cerussite [PbCO$_3$]; these corrosion products were also observed on the surfaces of the synthetic alloys used in our experiments. The type of lead oxidation product is very sensitive to the amount of water movement across the site and can be used as a guide to interpretation of degradation rates across an underwater archaeological site[17].

Conclusion

The use of synthetic alloys of tin with lead and antimony in corrosion experiments in open sea water and in artificial crevices has been shown to be able to reproduce similar morphologies and composition of corrosion products to those found on historic shipwreck artefacts. The data from acidity and chlorinity measurements of the crevices has enabled the appropriate Pourbaix diagrams to be developed for these synthetic alloys. The corrosion potentials of the synthetic tin alloys places the tin in the active corrosion region of the Pourbaix diagram, where soluble Sn(II) chloride complexes are the dominant ionic species. These measurements support the hypothesis that the outward diffusion of tin(II) chloride complexes from pits within the body of the metal has a major control on the mode of degradation. The combination of oxidative hydrolysis, internal pit pressure and the softness of the degraded alloy appear to cause the characteristic pustules on pewter artefacts.

Corrosion experiments have been used to demonstrate the passivating effects of anaerobic burial environments and good agreement between calculated short term corrosion rates and those observed after centuries has been found. Standardisation of desalination data to correct for the differing times of immersion in sea water has been shown to be a useful tool when comparing the varying degrees of degradation. The addition of antimony to tin causes major changes in the physical and electrochemical properties of the alloy which is very prone to selective corrosion of the tin-rich phases in aerobic sea water. Addition of tin to pure lead results in initial increases in corrosion activity but these fall off as the eutectic composition is approached.

Acknowledgements

References

1. J.N. Green, "The A VOC Retourschip Batavia wrecked Western Australia 1629: excavation report and artefact catalogue", BAR International Series 489, (1989).

2. I.D. MacLeod, "The effects of concretion on the corrosion of non-ferrous metals", Corrosion Australasia 10 (1985),10–13.

3. I.D. MacLeod, "Conservation of corroded iron artefacts – new methods for on-site preservation and cryogenic deconcreting", Int. J. Nautical Archaeology 16 (1987),49–56.

4. I.D. MacLeod, "Metal corrosion on shipwrecks: Australian case studies", Trends in Corrosion Research 1 (1993), 221–245.

5. I.D. MacLeod, "Electrochemistry and conservation of iron in sea water", Chemistry in Australia 56 (1989), 227–229.

6. R.J. Taylor, I.D. MacLeod, "Corrosion of bronzes on shipwrecks: a comparison of corrosion rates deduced from shipwreck material and from electrochemical methods", Corrosion 41 (1985), 100–104.

7. I.D. MacLeod, S. Pennec "The effects of composition and microstructure on the corrosivity of copper alloys in chloride media," ICOM Committee for Conservation, Preprints, 9th Triennial Meeting, Dresden Vol II (1990), 732–739.

8. I.D. MacLeod, "Conservation of corroded metals – a study of ships' fastenings from the wreck of HMS Sirius" Ancient and Historic Metals Conservation and Scientific Research, Ed D.A. Scott, J. Podany, B.B. Considine, Getty Conservation Institute, (1994), 265–278.

9. F. Schweizer, "Bronze objects from lake sites: from patina to 'biography'", Ancient and Historic Metals Conservation and Scientific Research, Ed D.A. Scott, J. Podany, B.B. Considine, Getty Conservation Institute, (1994), 33–50.

10. I.D. MacLeod, "Environmental effects on shipwreck material from analysis of marine concretions", Archaeometry: an Australasian Perspective (ANU Press), Ed. W. Ambrose & P. Duerden, (1982) 361–367.

11. I.D. MacLeod, "Identification of corrosion products on non-ferrous metal artefacts recovered from shipwrecks", Studies in Conservation 36 (1991), 222–234.

12. C.I. House, G.H Kelsall, "Potential-pH diagrams for the Sn/H$_2$O-Cl system", Electrochimica Acta, 10 (1984), 1459–1464.

13. C.J. Thwaites, "Antimony in soft solders – a review of the effects and its use in the soldering industry", Brazing and Soldering, (1986), 22–26, Special Publication No. 687, International Tin Research Institute.

14. A. Marshall, R. Piercy and N.A. Hampson, "The electrochemical behaviour of lead and tin alloys. I. Studies in nitrate electrolytes", Corrosion Science, 15 (1975), 23–34.

15. I.D. MacLeod and V.L. Richards – unpublished observations.

16. Handbook of Chemistry and Physics, 55th edition, CRC Press, Cleveland (1974), F190.

17. I.D. MacLeod, R. Wozniak, "Corrosion and conservation of lead in sea water" ICOM Committee for Conservation, Preprints, 11th Triennial Meeting, Edinburgh, James and James, London (1996).

Résumé

Le comportement à la corrosion, d'une série d'alliages synthétiques d'étain comprenant du plomb et de l'antimoine, en eau de mer, aérobique et anaérobique, a été étudié durant une année à l'aide de techniques électrochimiques, de la microscopie électronique et de la diffraction à rayons X afin de déterminer le processus de détérioration. La composition chimique des alliages a été choisie pour reproduire des compositions connues d'objets, ainsi que pour mettre en évidence les effets de la variation des teneurs de plomb et d'antimoine sur la microstructure et les caractéristiques électrochimiques subséquentes des matériaux. Une simulation de corrosion par crevasse a permis de montrer des variations importantes du pH du micro-environnement et de reproduire la micromorphologie et la minéralogie de plusieurs produits de corrosion de l'étain trouvés sur les objets d'épaves historiques postérieures au 17e siècle. La nature des produits de corrosion a été mise en parallèle avec les différentes étapes de dessalement des étains dégradés, rescapés d'épaves historiques.