Study of the corrosion of copper coins from the wreck of "The South China Sea No.1"

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Abstract.

The South China Sea No.1 is the wreck of the longest, largest and most preserved shipwreck site in China. It is a classic example of bireme construction and navigational technology. The artefacts located on the site may provide many secrets of the Silk Road on the sea. Therefore, the archaeological value is greater than its economic value. In order to know more about the craftwork and the state of the coppers in this wreck, this paper will examine the concretion and corrosion on the surface of copper samples obtained from the upper layer of South China Sea No. 1. The samples were analysed with metallographic microscopy, 3D video microscopy, X-ray diffraction (XRD),X-ray fluorescence （XRF) and scanning microscopy (SEM-EDS). The results show that the copper coin is tin-lead bronze, and the content of Cu is about 94%. The corrosion is mainly $Cu_2(OH)_3Cl$, Cu_2O, $Cu(OH)_2$, $Cu(OH)Cl$ and $Cu(SO_4)_2$. The concretion on the surface of the copper coin is rich, but the matrix becomes thinner. Lead (Pb) is scattered freely in the matrix. Tin (Sn) is high in the corrosion layer, which shows that some Cu has corroded. The electrochemistry of the corrosion was controlled by oxygen depolarization. Selective corrosion occurred between Cu and Sn, and the effect of Cl^- sped up the rate of corrosion in the electrochemical reaction. The results of the study can provide a reference for the protection of the copper artefacts excavated from South China Sea.

Key words: The South China Sea No.1, copper coin, archaeology

Introduction

Due to being in an underwater environment, undersea bronze has its own corrosion characteristics and corrosion products, which vary from bronze relics found on the land. With the high-speed development of underwater archaeology abroad, more and more resources have been put into the study of undersea relics in China. Internationally, several research projects studying the characteristics, composition, theory of corrosion and composition of the corrosion products in undersea bronzes have been conducted (Beccaria et al., 1982; Gettens, 1933; MacLeod, 1991;MacLeod, 1982;Scott, 2002). Gettens (1964), for example, identified cuprous sulphide (Cu_2S) and digenite ($Cu_{18}S$)in the corrosion products on copper nails recovered from a shipwreck in the Mediterranean. Copper (II) sulphate (CuS)was identified by XRD on a fragile black-blue bar from the wreckage of Herminie. According to studies of the corrosion products on undersea bronze by MacLeod (1985), North(1987) and Nord(1993),copper oxide(Cu_2O), cuprous chloride (CuCl), chalcanthite ($CuSO_4 \cdot 5H_2O$), brochatite ($Cu_4SO_4(OH)_6$), lead carbonate ($PbCO_3$), lead sulfate ($PbSO_4$), stannic oxide (SnO_2), and CuS are also common corrosion products.

Currently, research on the conservation of bronze artefacts in China is still lacking. Despite the development of underwater archaeology internationally, more and more bronze artefacts are being recovered but domestically, the question of how to protect them is still a problem.

Researchers are therefore using The South China Sea No.1 as a case study to research the conservation of bronze relics. This site provides a typical sample for the study of ancient Chinese shipbuilding technology and marine technology. The associated artefacts can also potentially unlock the key to many secrets of the marine Silk Road. The archaeological value of the cultural relics at the South China Sea No.1 site is much greater than the economic value. At present, the excavation of the South China Sea No. 1 and the protection of the bronze relics housed at the Marine Silk Museum not only provide valuable historical information about wreck protection but also provide a strong reference for the study of marine water relics. It will provide reliable support forthe protection of our marine cultural resources.

Analytical instruments

The methods utilised to analyse the concretion on the bronze surface and the corrosion products included: an Olympus metallurgical microscope from Japan; the KSTAR Company's HIROX KH-3000 3D video microscopy; Japan the Science RINT2000 X-ray diffractometer (copper target, slit DS = SS = 1 °, RS = 0.15mm, voltage 40kV, current 40mA); scanning electron microscopy and energy dispersive spectroscopy; Hitachi S-3600N scanning electronic microscope (SEM) and the EDAX Genesis 2000XMS X-ray energy dispersive spectroscopy (EDS) (SEM-EDS); and XPS.

Fig.1a: copper coins from The South China Sea No.1.: (X. Tian).

Results and analysis

Coins surface morphology analysis

Representative samples were taken from the concreted copper coins (Fig. 1a). 3D video microscopy was used to observe the surface morphology of the copper coins and the results are shown in Fig.1b.A metallographic microscope was used to observe the cross-section of the sample coins with the results shown in Fig.1c.

Fig.1b: The 3D video microscopic image of the concretion and corrosion on the surface of the copper coin.: (X. Tian).

Fig.1b demonstrates that the coin has an uneven distribution of black, brown and green coloured material on the surface. There are also varying degrees of spots, salt crystallization and a dark texture on the surface.

Fig.1c: The metallographic dark field image of the cross section of the copper coin.: (X. Tian).

Results of the metallographic microscopy (Fig.1c) identifies that the outside of the coins are corroded. The results also establish that a uniform phase is formed within the coins. This includes the yellow area interspersed with many black spots located inside the coin matrix, also seen in Fig.1c. The grey concretion can only be found on the edge of the thin layer and the corrosion products are located between the concretion and the metal matrix. Additionally, the coin is thin.

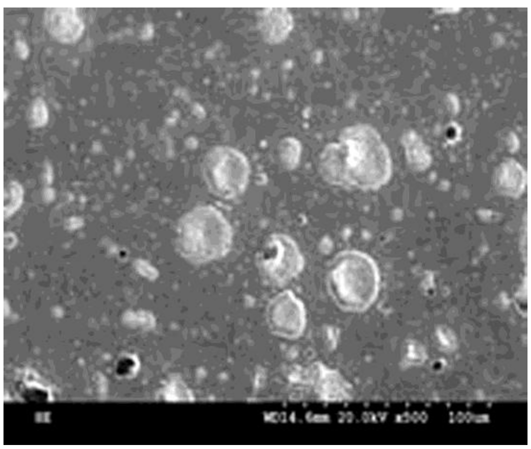

Fig.2a: SEM image of the metal matrix of the copper coin.: (X. Tian).

Chemical composition of corrosion products

The corrosion products on the coins from the South China Sea No. 1were analysed by XRD. The results are shown in Table 1. The major corrosion products include basic cupric chloride [$Cu_2(OH)_3Cl$], cuprite (Cu_2O), copper hydroxide [$Cu(OH)_2$], cupric hydroxyl chloride[$Cu(OH)Cl$], and cuprous sulfate [$Cu_2(SO_4)$].

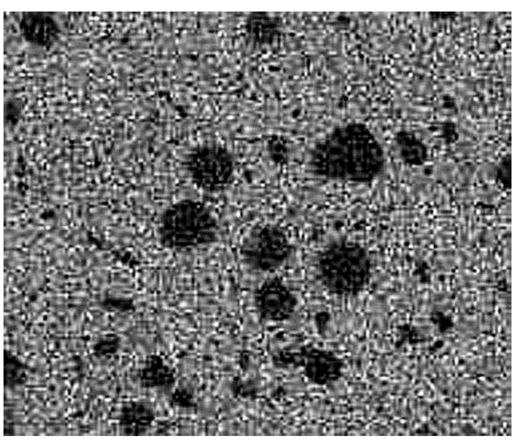

Fig.2b: distribution image of Cu.: (X. Tian).

The composition and structure of the matrix of the coins

The metal matrixes of the coins were analysed by SEM and EDS to investigate the composition and structure of the substrate shown in Fig.2. Fig.2a shows the SEM images of a sample coin's metal matrix. Figs 2b, 2c, and 2d provide an example of the distribution of Cu, Pb and Snin the metal matrix, respectively. The SEM image of the copper coin metal matrix shows uneven grey spots, which are Pb-rich pockets distributed across the coin. Except for these Pb areas, Cu and Sn are evenly distributed throughout the matrix. EDS results show that the composition of the coins is as follows: Cu is about 94%, Pb is approximately 4%and Sn is only about 2%.

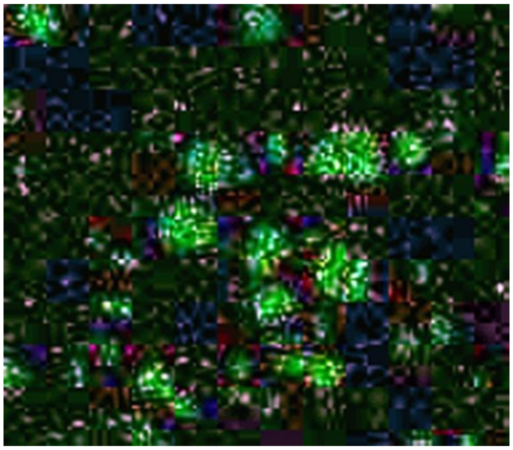

Fig.2c:The distribution image of Pb.: (X. Tian).

Analysis of the corrosion process

While cutting the edge of the coins, only a little metal matrix was observed. The first step was to observe the outside of a cross-section of the coins through SEM and then analyse the elements of the different colour regions identified. The analysis results are shown in Fig.3 and Table 2.

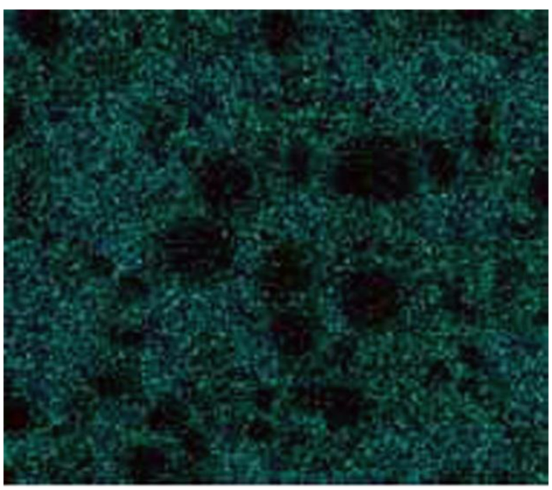

Fig.2d: distribution image of Sn.: (X. Tian).

Fig.3 shows that Zone 1 is a black, loose surface layer along the outside of the coin. This is the concretion layer, which contains a small amount of Cu, but no Pb and Sn. Zone 2 is a white layer of uneven thickness, which contains S and Pb, and therefore may be $PbSO_4$. Zone 3 is a greyish-black, banded structure, containing S, Pb, Cl and Cu, which may be $PbSO_4$ and copper chlorides. Lastly, Zone 4 is grey and the largest area. This section contains Cu, Pb, Sn, Si and Cl, which corresponds closest to the coin metal matrix.

Table 2 shows that the main elements in the corrosion products are Cl and S. After comparison of the results, Zone 2 contains the greatest amount of Pb, Zone 3 contains the greatest amount of Cu and Zone 4 contains the most Sn. Therefore, the Cu in the coin has preferentially corroded.

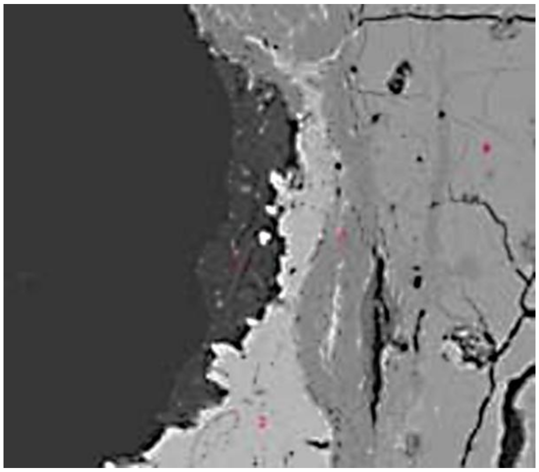

Fig.3: SEM image of the cross section of the outer layers of the copper coin.: (X. Tian).

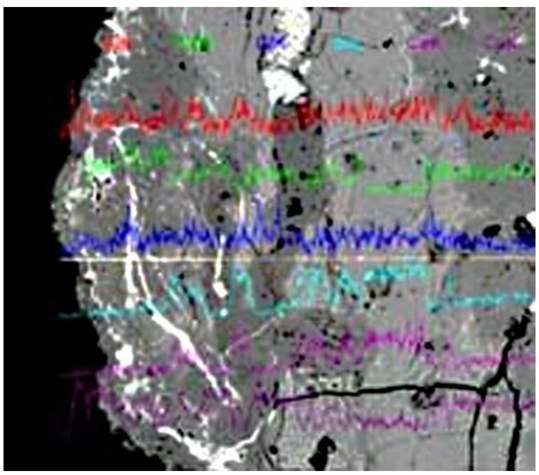

Fig.4: The content line of different elements in the cross section of the copper coin.: (X. Tian).

In order to observe the change in the content of each element from the outer surface to the inner regions of the coin, SEM analysis was conducted. The results are shown in Fig.4. Fig.4 shows that the content of Cu, Sn and Ca change significantly in the white area, while the content of Si, Pb and Cl change only slightly. Pb is mainly found in Zone 2, while Sn occurs mainly in Zone4. Overall, the Cu content Cu changes in most zones and in the greyish black zone, Cu is greater, which maybe the residual Cu metal matrix.

Discussions

The corrosion layer found on thebronze artefacts from The South China Sea No.1 shipwreck was mainly turquoise in colour. The typical powdery rust coloured corrosion that falls off when touched was uncommon on the copper coins. The corrosion products identified were $Cu_2(OH)_3Cl$, Cu_2O, $Cu(OH)_2$, $Cu(OH)Cl$, $Cu(SO_4)_2$.

Copper chloride was one of the main corrosion products (e.g.$Cu_2(OH)_3Cl$ and $Cu(OH)Cl$) identified. Chlorine easily induces bronze corrosion, so it is important to take the proper measures to remove as much chloride as possible, via proper desalination to effectively stabilise the metal. The analysis of the corrosion products provides data that will assist in deriving better methods for later desalination work. From the presence of copper chlorides (i.e. $Cu(OH)$ Cl and $Cu_2(OH)_3Cl$) and cuprite (Cu_2O) corrosion products, it can be deduced that the bronze in the South China Sea No.1 was primarily in anaerobic marine environment, which included Cl^- and SO_4^{2-} in solution. Where oxygen was more abundant loose concretion formed on the outside of the coins. There are, however, some instances when oxygen was sealed in the space between the original metal surface of the coins and the loose concretion. Thus, the oxygen depolarization controlled the electrochemical corrosion of the bronze. In this type of environment, Sn has a lower electrode potential than Cu, so it corrodes first, with the effect of Cl^- speeding up the rate of corrosion by combining with Cu and Sn ions to form new corrosion products.

Conclusion.

1.The copper metal matrix contains mainly Cu, Sn and Pb at a ratio of 47:1:2, respectively.

2.The copper corrosion products mainly include: $Cu_2(OH)_3Cl$, Cu(OH) Cl, Cu_2O, $Cu(OH)_2$ and $Cu(SO_4)_2$。

3. Selective corrosion occurred between Cu and Sn in the bronze coin and the presence of Cl^-increases the rate of corrosion in the electrochemical corrosion reaction.

Table 1

sample	Main composition
NHTQ-1-a	Cu_2（0H）$_3$Cl、Cu_2O
NHTQ-1-b	Cu_2（0H）$_3$Cl、Cu_2O
NHTQ-1-c	Cu（0H）$_2$、Cu（0H）Cl、Cu_2O
NHTQ-1-d	Cu（0H）$_2$、Cu（0H）Cl、Cu_2O
NHTQ-2-b	Cu（0H）$_2$、Cu（0H）Cl、Cu_2O、Cu（SO_4）$_2$
NHTQ-2-a	Cu（0H）$_2$、Cu（0H）Cl、Cu_2O、Cu（SO_4）$_2$

Table1:The XRD results from the analysis of the corrosion products from the copper coin from the South China Sea No. 1 shipwreck.: (X. Tian).

Table 2

No.	Elements（Wt%）										
	Mg	Al	Si	S	Cl	K	Ca	Fe	Cu	Pb	Sn
1	3.0	17.4	36.8	7.7	1.8	3.9	2.6	21.7	5.1	—	—
2	—	—	—	3.6	—	—	—	—	—	96.4	—
3	—	—	—	40.5	1.7	—	—	—	43.1	14.7	—
4	—	—	1.8	—	0.7	—	—	—	5.7	23.1	67.7

Table 2:The elemental distribution of the cross section of the outer layers of the copper coin.: (X. Tian).

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Biography.

Xing-ling Tian *is a conservation researcher who holds a doctor's degree of Materials Science and Engineering from Beijing University of Chemical Technology. In 2003,* Xing-ling Tian *joined the Chinese Academy of Cultural Heritage (State Administration of Cultural Heritage Center of Underwater Cultural Heritage).In 2006, became a research associate. Past research interests have been predominantly concerned with the conservation of metal and wood, developing and applying research to new materials and techniques and currently I am focused on the conservation of underwater cultural heritage.*