Analysis of a gilded and corroded archaeological bronze, Shark Bay Western Australia

A report on the examination for the finders

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Heritage Conservation Solutions
Analysis of corrosion & materials deterioration
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Gilded bronze Chinese Buddha as found

Background

Heritage Conservation Solutions were contacted by the Honorary Associate of the WA Museum Bob Shepherd to assist colleagues with the identification of a recent archaeological bronze recovered from a site near Denham, in the Shark Bay region of Western Australia. The bronze was found by Shayne Thomson and Leon Deschamps and is illustrated on the cover page of this report. The bronze was examined using a binocular microscope at up to x 40 magnification under white and raking light. A summary of the key observations is listed below:

1 There are a series of striations in the gilding that are consistent with the application of a gold mercury amalgam. The corrosion pattern on the bronze indicates that it has a fine recrystallized structure that is consistent with the object having been fire gilded. In the heating process the microstructure has changed from being an as-cast dendritic structure, as seen in Figure 1 to a recrystallized and very fine-grained leaded medium bronze, as seen in Figure 2.

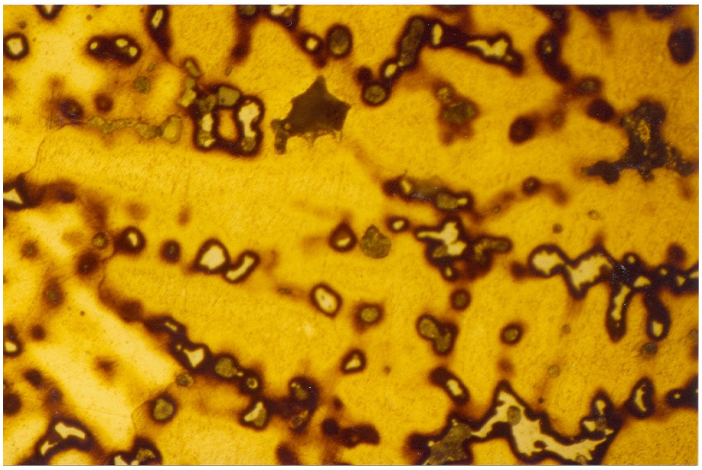

Figure 1: Shipwreck leaded tin bronze from the wreck of the American China trader *Rapid* (1811) showing cored dendrites of the α solid solution with the light-coloured areas being the (α+δ) eutectoid and the dark grey particles are the lead rich phases

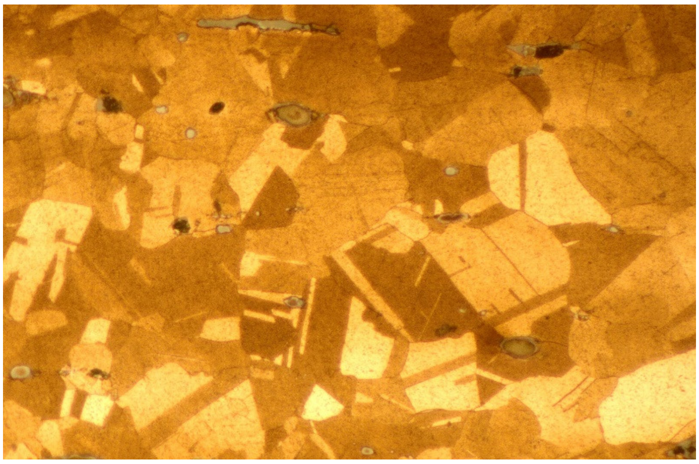

Figure 2: Recrystallised microstructure of a copper alloy, showing twinned grains and lead inclusions, elongated along the lines of mechanical working.

2 The phase diagram for copper and tin is shown below in Figure 3.

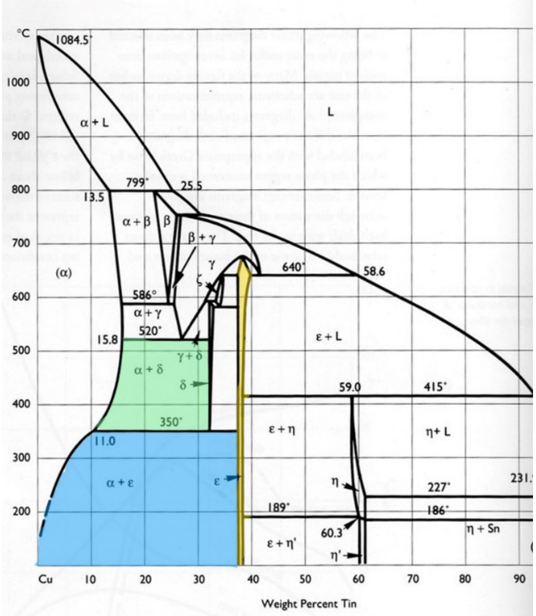

Figure 3: The phase diagram for copper and tin

It is likely that the gilded bronze Buddha has between 10-15 wt.% tin and perhaps around 1-2.5 wt.% lead. By reading the abscissa and following the 10% line up the ordinate, the parent alloy melts at around 1000°C. As the molten metal cools the primary phase to precipitate out is the α-copper rich phase. As the copper solidifies the resultant mixture becomes richer in tin. A series of solid phases form and as the temperature falls the eutectic mixture of α+δ forms (the green coloured area) and this is the dominant phase in the metal structure.

3 There is a fine patina of chalcocite, Cu_2S, over the major part of the surface which is due to the object having been in an anaerobic microenvironment for a considerable period. Sulphate reducing bacteria convert SO_4^{2-} ions into S^{2-}, as they consume the oxygen for metabolic purposes. As the bacteria oxidize food the sulphur atom is reduced from the +VI to the -II state and this metabolic by-product forms the very stable and insoluble copper (I) sulphide chalcocite -see Figure 4.

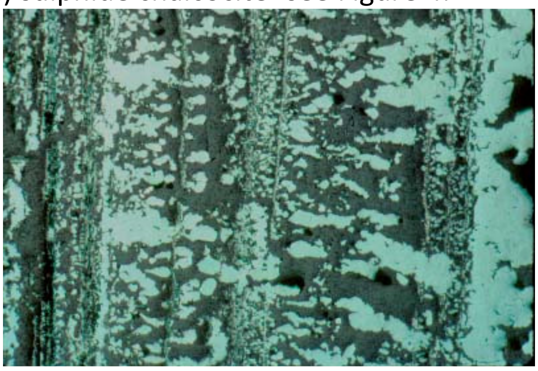

Figure 4: Chalcocite (Cu_2S) deposited into the cells of American Oak from the wreck of the *Rapid* (1811) – full width of image 2.2 mm

4 There are a few areas where around the granulations and the general decorations associated with convolutions of the surface, there are localised outbreaks of light grey corrosion products and this is indicative of corrosion of the eutectoid phase under low oxygen conditions. Under this environment there is thermodynamically controlled corrosion of the tin-rich phase which results in mobilisation of tin as a tin (II) chloride complex and precipitation as a mixture of tin (II) and tin (IV) corrosion products. Some of this form of localised corrosion has occurred underneath the chalcocite patina and has partially replaced the dominant patina. **These corrosion products show that the object has been in a mixture of microenvironments over the burial period** – see Figure 5**.** In these regions of exposed tin corrosion products there are also lead degradation products present such as the white basic lead carbonate hydrocerussite, $Pb_2(CO_3)_2(OH)_2$.

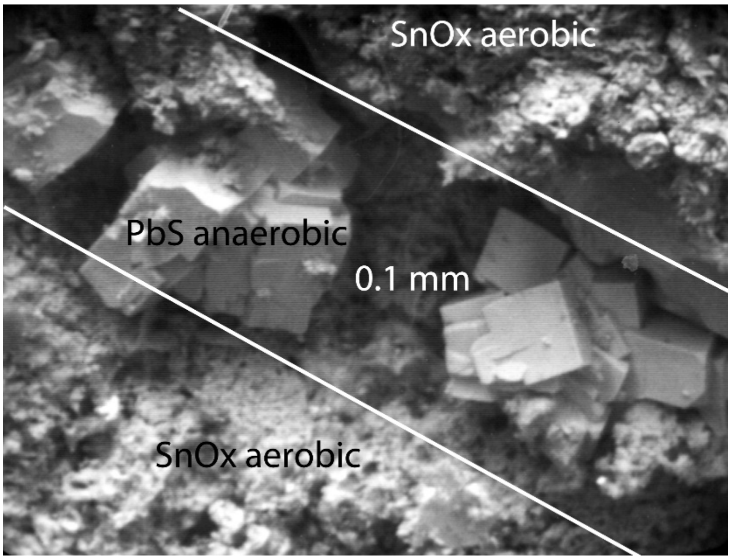

Figure 5: Scanning Electron Micrograph of a section of pewter from the wreck of the *Vergulde Draeck* (1656), showing the sandwich of an anaerobic between two aerobic microenvironments.

5 At various points on the Buddha there are shrinkage lines due to the rapid cooling of the molten metal as it hits a cold section of the mould. This indicates that the medium into which the bronze metal was poured was not heated to any significant temperature prior to the casting process. Near the gilded decorations of a series of inter-connecting semi-circular lines, there is an area of blue-stained tin corrosion products and nearby an area rich in the ruby-red cuprite (Cu_2O) phase from corrosion of the α-phase during a period of exposure to much high levels of dissolved oxygen. Near this area is what appears to be a Chinese character like a stylised “M” with an outstretched arm half way up the right-hand side of the “M” that terminates with an upward flourish.

6 Near the reverse side of the head there are a series of cupule indentations that are consistent with the artisans removing the object while the mould was still warm. On finding that there were casting defects, in the form of gas porosity on the surface, these areas were peened, and this would have resulted in mechanical deformation that would have hardened the object and strengthened the connection of the head to the rest of the body.

7 There was a marked indentation on the lower left leg and when viewed in profile it is apparent that the metal had NOT been lost in this incident, but had on the contrary, been moved into a conformational horizon of an upwelling. This movement is akin to the formation of a crater after the impact of a meteorite. It is likely that this accident happened before the object had come to room temperature and may have occurred during an accidental drop after it was removed from the gilding furnace.

8 There are concave and convex lines on either side of both knees as the rear facing areas. These incisions form part of the gilded decoration and are consistent with a deliberate process of adjusting the as-cast angle of the legs to ensure that the Buddha was stable on its own two feet.

9 In the regions of the distal end of the hands, there are two very finely made location lugs for the insertion of the Index fingers, one pointing upwards and the other pointing downwards. It appears that the glue holding in inserts, such as ivory, have been microbially attacked and this has allowed the dislodgement of the said objects. It is recommended that fine sieving of the site be conducted in order to try and locate the missing fingers.

10 There was one large sized crystal of azurite, $Cu_3(CO_3)_2(OH)_2$, approximately 0.8 mm across, found lying near an edge of high relief. This is consistent with the crystal having grown from the accumulation of water run off and it was on the upper facing surface of the sculpture. This observation is a very clear indicator that the object was not recovered from a shipwreck site where copper hydroxy chlorides, of the general formula $Cu_2(OH)_3Cl$, are found in great abundance. In more than 200 mineral analyses conducted on shipwreck bronzes no sample of azurite have been found. There was also a large black mineral grain that was consistent with it being the mineral ilmenite, $FeTiO_3$, which is well distributed in the sand dunes around Denham.

11 Comparison of the extent of corrosion on other materials recovered in the general environment of the find are characterised by a patina that is dominated by cuprite and there are only medium intensity areas of chloride induced pitting corrosion on the surfaces of the copper alloy objects. The archaeological context is characterised by a generally slow corrosion rate due primarily to the lack of water in the sandy soils.

Conclusion

Having examined the surfaces of the gilded bronze Buddha it is my considered view that the object is NOT a replica but a genuine archaeological bronze object. I have examined and treated more than 120,000 archaeological copper alloy objects and have over a period of 40 years developed some skills in the identification of corrosion products and in the way in which metallic objects interact with their microenvironment to produce mixtures of minerals that attest to the changes that have taken place over many centuries.

It is not possible, even with the most sophisticated chemical methods, to develop a complex patina such as found on the Shark Bay bronze object. The fine-grained chalcocite patina is very coherent and is not rubbed off with handling and this attests to the long time it has taken to corrode the underlying bronze and to produce a tightly adherent mineral deposit. If the object had been placed in an artificial anaerobic microenvironment the dark grey to black mineral would be powdery and more uniform.

To find one grain of azurite on one part of the surface attests to the specific microenvironment needed to bring about mineralisation of this copper hydroxy carbonate. An artificial patinating agent can produce this mineral but in grains that are microns in thickness and not fractions of a millimetre.

The complex secondary mineralisation of the tin and mixed lead corrosion layers is due to a change in environment from being anaerobic to partially oxygenated and this brings about selective corrosion on the eutectic $(\alpha+\delta)$ phase, which is higher in tin content and therefore more thermodynamically active which makes it more prone to corrosion. Owing to the restricted nature of the availability of water the corrosion products were not lost to the burial environment but remained on the surface of the object.

The staining of the sand grains by copper corrosion products only goes to the first sand grain, whereas ancient Egyptian bronzes have 3-6 grains thickness of staining. The desiccated Shark Bay environment is not dissimilar to Egypt and based on these observations it can reasonably estimated that the object has been in that environment for very many decades i.e. it has not been planted on the site, in an attempt to lure metal detector operators into the belief that they have found some ancient object.

The period of manufacture is to be determined largely on art history and stylistic evidence.

End of Report