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INVESTIGATION AND REPLICATION OF THE SURFACE MICROSTRUCTURE OF EARLY CHINESE BLACK BRONZE MIRRORS

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ABSTRACT

Many ancient Chinese bronze mirrors have survived with their original surface decorations intact, particularly those with glassy black surface coatings. The microstructures and compositions of cross-sectional samples from ancient mirrors have been analyzed with optical and electron microscopy and synchrotron x-ray fluorescence. The core has a two-phase metal structure while the surface shows evidence of selective dissolution of copper from the α (Cu-rich) phase. The α phase regions are replaced pseudomorphically by a mineral product with the δ (Sn-rich) phase remaining metallic. A fundamental study of the electrochemistry of the copper-tin system has given information on the conditions under which selective dissolution of copper takes place. Electrochemical polarization has been used to drive the copper dealloying process in cast high-tin bronze. The resulting microstructure is similar to the dealloyed microstructure observed in the ancient samples.

INTRODUCTION

Certain ancient Chinese bronze mirrors have survived for 2000 years or more with little obscuration of their original surface decorations. These mirrors have been the subject of scientific study in both the East and West due to their unusual corrosion resistance.¹⁻⁹ Bronzes with glassy black patinas seem to be particularly well-preserved.² Other mirrors have dark green, grey or brown patinas. Well-preserved silvery, metallic looking mirrors have also been reported.⁹

Chinese mirrors are "high-tin" alloys with an average composition of 70% copper, 25% tin and 5% lead.^{2,9} High-tin bronze, cast and allowed to cool slowly, develops a two-phase microstructure consisting of the alpha (α , copper-rich) and delta (δ , tin-rich) phases. The microstructure is dependent on composition and cooling rate. Because lead is insoluble in this material, it can usually be seen as spheroidal particles.

High-tin bronze artifacts usually have an intact two-phase metal core and at least one surface layer.^{2,8} A "glassy" layer is often found as the outermost surface layer on black bronze mirrors. It is non-conductive and contains silicon and iron, elements which are not found in the bulk metal. No organic coating has ever been found on these objects.²

However, the surface layer most commonly found on high-tin bronze mirrors is called the "altered region." This layer is continuous with the core bulk metal. In this region, the α phase has been replaced by a mineral product, while the δ phase remains metallic.

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Spectroscopic measurements of the surface find that it is richer in tin than the bulk metal.^{2,5-9} It has been suggested that mercury may have been used to enrich the tin on the surface of these objects.^{5,8} Zhu and He⁸ and Chen *et al.*⁵ have found references in the ancient literature to the use of a tin-mercury compound to polish Chinese mirrors. Meeks puts forth an alternative explanation involving selective dissolution of the high-copper α phase yielding a higher tin to copper ratio at the surface.⁹ Selective dissolution is also referred to as "dealloying."

In *The Freer Chinese Bronzes*, R. J. Gettens describes some Shang and Zhou high-tin bronze vessels and early Chinese bronze mirrors that have a well-preserved compact green surface patina called "water patina."¹⁰ Gettens showed that these objects also have an altered region, and that tin oxide (SnO_2 , possibly hydrated) is the mineral that replaces the α phase. The α phase is replaced pseudomorphically. He suggests that the observed microstructure could be formed in acidic burial conditions. This conviction is born out by the thermodynamic calculations that are represented in potential-pH (Pourbaix) diagrams.¹¹ In soils of low pH and oxidizing conditions, the copper in the alpha phase would be expected to dissolve while the tin should be incorporated into an oxide. In this paper, this assertion is examined using electrochemical techniques. With these techniques, oxidizing conditions can be ensured by controlling the electrode potential of the bronze sample. Dealloying experiments were carried out in two solutions: dilute acid and an ammonia solution. The latter was used to determine the effect of copper complexation on the resulting microstructure.

EXPERIMENTAL

Two kinds of sample were used in this work. Cross-sectional samples from ancient artifacts were investigated to determine the character of the surface layers. Secondly, modern cast high-tin bronze pieces were subjected to dealloying treatments for comparison with ancient pieces.

The cross-sectional samples from three ancient mirrors were supplied by the Freer Gallery. These samples were mounted in epoxy and polished down to a mirror finish. The sample shown in this paper is from a fragmentary Han mirror donated to the Freer Gallery by Mr. Kajima of Tokyo.

The modern samples were from a boule cast at Brookhaven. These samples contained 25 % tin by weight in copper (Cu-25Sn). No lead was added. The metals were melted together and chill cast. The experimental samples were annealed at approximately 480°C for 16 hours in a reducing environment ($\text{Ar}-1\%\text{H}_2$). The resulting microstructure consisted of α and δ phases of about 50% each. The bronze pieces were approximately 0.5 by 0.5 by 1 cm in dimension. One face was polished with 1 μm diamond paste to simulate an ancient well-polished mirror face. A hole was drilled into one end and a steel rod was inserted into the hole to make electrical contact. Shrink-tubing was placed along the length of the rod and epoxy was used to insulate the bronze-steel interface.

The dealloying experiments were conducted in a beaker that was covered to minimize solution evaporation. The bronze "working" electrode was held at a constant DC potential versus a copper pseudo-reference electrode. This potential was periodically checked using a stable mercurous/mercuric sulfate (MSE) reference electrode. High purity copper was used for both the pseudo-reference and the counter electrode. The current flowing between the counter electrode and the working electrode was recorded as a function of time.

Two solutions were used: 0.01M sulfuric acid and 1M $[\text{NH}_3 + \text{NH}_4^+]$. The latter was a 1:1 mixture of 0.5M $(\text{NH}_4)_2\text{SO}_4$ and 1M NH_3 .

The current/voltage characteristics of copper, tin and Cu-25Sn were measured with a three-

electrode system under deoxygenated conditions in a closed glass cell. Potentials were controlled relative to a stable MSE reference electrode. The measurements, called cyclic voltammograms, are conducted by ramping the potential on the working electrode at a constant rate and measuring the current response. A low current at a particular potential indicates that the working electrode is undergoing very little change. Conversely, a high current indicates that metal dissolution, oxide formation, or gas evolution is occurring on the surface of the electrode.

X-ray fluorescence (XRF) measurements on the cross-sections of ancient samples were conducted on Beamline X-26A at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. The increased intensity of synchrotron x-rays allows for detection on the order of one part per million of mercury.

All of the samples were investigated with optical and scanning electron microscopy. All of the SEM micrographs in this paper were taken using the backscattered electron detector of the electron microscope (this mode is sensitive to atomic number).

RESULTS

The microstructure of ancient Chinese mirrors has been reported by other researchers.^{2,4-9} The current work confirmed the two-phase α - δ structure with lead globules. The δ phase is seen as the light grey material in Figure 1. The α phase is a darker grey and is enclosed in a matrix of δ at the bottom of the figure. The altered layer can also be seen clearly in the figure. The light grey δ phase matrix continues to the top edge of the image. Also visible are α phase-shaped areas which appear much darker. Higher resolution images (not shown) indicate that these areas are filled. Backscattered electrons are sensitive to the atomic weight of the material. The dark appearance of the material which has replaced the α phase suggests that it is a material with a low average molecular weight such as an oxide.

Figure 2 is an x-ray fluorescence spectrum that was taken at the NSLS. The arrow marks the position of the main mercury peak. No mercury was detected. The detection limit is on the order of 1 ppm.

Figure 3 shows SEM micrographs of the cross-sections of two of the modern electrochemically dealloyed samples. Again, the two-phase structure is visible. The altered

Figure 1. Cross-section of the surface of a Chinese Han black mirror (FGA: LRN 2191) showing the characteristic microstructure

Figure 2. Synchrotron XRF spectrum of a spot on the surface of a Chinese black mirror. The arrow indicates where a mercury peak would appear if mercury were detected.

region is visible on the right side of each image. The thickness of the dealloyed region can be seen to be dependent on the direction of the α -phase needles with respect to the surface. Figure 3(a) was dealloyed in sulfuric acid, while Figure 3(b) was treated in ammonia. The α phase regions appear to be filled in the case of acid dealloying and partially filled in the case of ammonia dealloying.

The top face (polished prior to dealloying) of each of the samples in Figure 3 is shown in Figure 4. The α phase regions of the piece that was treated in sulfuric acid (Figure 4(a)) can be seen to be filled with another material. The appearance is like that of dried, cracked earth. The ammonia-treated sample (Figure 4(b)) appears to be solely δ phase: the α phase regions are empty.

Figures 5(a) and (b) show the current/voltage characteristics for copper, tin and Cu-25Sn

Figure 3. Cross-sections of the surfaces of samples dealloyed in (a) sulfuric acid and (b) ammonia showing the bulk metal structure and the dealloyed region (on the right in each micrograph). (SEM, backscattered mode)

Figure 4. Faces (polished prior to dealloying) of samples dealloyed in (a) sulfuric acid and (b) ammonia. In (a), a deposition product that looks like cracked earth is visible in the α phase holes. Only the δ matrix is seen in (b). (SEM, backscattered mode)

in the two solutions. The vertical, dotted lines indicate the potential at which the dealloying experiments were run. At these potentials, the tin is relatively inactive as indicated by the low current. The copper current is high which indicates a combination of Cu^{2+} dissolution and oxygen evolution, in this case. The bronze current is lower than that of the copper.

Figure 5. Current/potential plots for copper, tin and Cu-25Sn in (a) sulfuric acid and (b) ammonia. The vertical, dotted line indicates the potential at which the dealloying experiments were run. The horizontal scale is referenced to an MSE reference electrode.

DISCUSSION

The results suggest that the formation mechanism of the surface microstructure in ancient bronze mirrors is due to the dealloying of copper from the α phase. This is consistent with the suggestions of Meeks⁹ and Gettens¹⁰. In oxidizing conditions, the α phase would be expected to dissolve.¹¹ This α removal was demonstrated in both sulfuric acid and ammonia. This phenomenon could have taken place as a result of burial in acid solutions (e.g., Gettens¹⁰).

No mercury was found in the ancient mirror sample tested by synchrotron XRF. This result is also consistent with the dealloying mechanism, but does not completely rule out the hypothesis of Zhu and He⁸ and Chen *et al.*⁵ that a mercury polishing compound was used to increase the surface Sn/Cu ratio. This is because problems can be encountered with the detection of mercury. For example, Zhu and He⁸ report that no mercury was detected on a sample that had been polished with a mercury-tin compound after a passage of only three years. One of the authors (WTC) has also found the detection of mercury troublesome.

The nature of the material which replaces the α phase is likely to be affected by the chemical species in the solution. In the acid solution, a material can be seen to have replaced the α phase throughout the altered region. However, the piece treated in ammonia solution displays a replacement material only within the sample near the bulk metal. The material replacing the α phase may in turn affect the color of the final piece. It was observed that the pieces treated in sulfuric acid were a darkish grey color after treatment. The ammonia-treated pieces retained a more silvery, metallic appearance. Further work is underway to characterize the effect of solution on sample color and the nature of the α replacement material.

CONCLUSIONS

1. A microstructure similar to that found on ancient high-tin bronzes has been reproduced by electrochemical dealloying. An altered region was formed in which copper was removed from the α phase.
2. No mercury was found which is consistent with the suggestion that the increased tin to copper ratio at the surface was not formed through the use of mercury.
3. The dealloying solution affects the deposition of the oxidation product in the void left by the dissolution of the α phase. This may in turn affect the color of the surface.

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