Close up to the Surface: Reflections on a Preliminary Forensic Study of Four Chinese Bronze Mirrors from a Hong Kong Private Collection

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Abstract

This article presents an objective, forensic study undertaken within the HKU Architectural Conservation Laboratory (ACLab) conducted on 4 very different bronze mirrors from a private collection. They nominally cover the period from the Warring States (475-221BC), Han (206 BC to 220AD) and later Song (960-1279AD) dynasties. Comprehensive, non-invasive, analytical methods and techniques were applied in this endeavour, including microscopic observation of tool marks, patina, corrosion and any residual archaeological evidence. Ultraviolet radiation examination as well as pXRF analysis of the bronze alloy, corrosion products and any earthen encrustations were conducted. The combined results have revealed key alloy information of those four mirrors along with surface patina morphology and details of the corrosion products and residual surface archaeology. Three of the mirrors from the Warring States, late Han, and Song dynasties appear to be genuine artifacts based on the available forensic evidence presented. One other nominally also from the Warring States period has some indications of veracity but requires further study. The two Warring States mirrors appear to have been heavily cleaned, polished and treated with abrasives in modern times. This study shows that use of modern technologies for forensic investigation and evaluation of bronze mirrors that otherwise lack verifiable background information as to their origin can be a useful adjunct to expert appraisal.

Introduction

Chinese bronze mirrors from antiquity, in all their variety and forms, are valued cultural heritage items. Provenance in most cases is sparse. The exceptions are for well documented cases from certified excavations where proper archaeology is possible or from mirrors that come up for sale in top auction houses from reputable collections where provenance usually relates to an ownership history that may go back decades (but may not of itself donate veracity). The archaeological detail, necessary for more meaningful and contextual historical evaluation, is normally missing in such cases. Nevertheless, undertaking a proper scientific evaluation of such objects with respect to issues such as metallurgy, corrosion products, encrustations, wear and tear, repairs, cleaning and any trace archaeology still provides valuable insights into the true nature of the objects and may provide some confidence to owners. This is independent of any stylistic and compositional elements in the design that often provide vital clues to authenticity and period.

Mirror history in China

There are different opinions on where the first idea to make bronze mirrors by the ancient Chinese originated. Modern scholar Liang Shangchun [1] thought the ancient Chinese got the inspiration of creating a reflective surface to see the world from looking at still water in a lake or pond. Gradually, bronze basins and later polished bronze plates were developed for reflection. The earliest recognisable Chinese bronze mirror was unearthed in Gansu Province and has been dated to the Neolithic period's *Qijia* culture. Over the subsequent 4000 years of history, Chinese bronze mirror design, technology and prominence experienced several important time periods including the three most important: the Warring

States (475-221BC), the Han (202BC-220AD) and the Tang (618–907). By the time of the Song dynasty (960-1279AD) the Mirror industry was in decline though this period was the most varied in terms of mirror shape, even if design typically simple. This opinion is based on the distinctive characteristics, artistic design and material quality and the numbers of surviving examples from these periods.

The Warring States was a developing period of bronze mirror refinement, indicated by diverse artistic styles and delicate and intricate decoration. The Han dynasty was a period when the bronze mirror industry was flourishing as evidenced by the vast numbers of mirrors from this period that have come to light even if the execution of their designs were of lesser quality. In the Tang dynasty, in terms of shape, size, pattern and various decoration techniques such as with lacquer and mother of pearl, bronze mirrors were much more varied and sophisticated but again the surface precision and fineness does not match the excellence of the Warring States.

The bronze mirror industry started to decline during the Song dynasty as indicated by the significantly less numbers uncovered via archaeological excavations and the more simple designs compared to the preceeding Tang dynasty [2]. Some scholars believe that the decline of the mirror industry during the Song is related to wars and a reduction of copper mining. However, Zhang [3] has a different opinion, considering the reason for the lack of even basic decoration on Song mirrors being the result from the prevalence of adopting a 'simple life' philosophy of that time.

Mirror casting

In China, bronze mirrors were manufactured via the commonly adopted clay mould casting technique. The model, together with desired inscribed decoration, was made first and the mould was second [3, p. 32]. An archaeological excavation of a mirror workshop dated to the Western Han dynasty in Shandong province, P.R. China [4] proved this practice was employed. Before clay moulds, stone moulds were used [5]. There is no evidence found to indicate that the lost wax technique was used by the ancient Chinese to make bronze mirrors, perhaps due to the simple forms.

Mirror alloys

Like other ancient bronzes, a bronze mirror is an alloy that contains various fractions of copper, tin and lead. Although historic records did not specifically mention lead in their formulae, lead is commonly detected. According to the "six formulae: for making bronze for different uses given in K'ao Kung Chi 考工記 by Tai Chen, the ratio for making mirrors and specula is 50% Copper and 50% tin. However, this 50:50 ratio is not observed in extant studied mirrors based on modern scientific appraisal and metallurgical analysis. Qiu [2] pointed out that the scientific data collected from known bronzes is very far removed from the alluded 50:50 ratio. Chase et al. [6, p. 21] revealed that bronze mirrors typically contain approximately 70% copper, 25% tin and 4% lead. Barnard [7,table 9] gave the average percentage of each element, for a sample of both attested and unattested bronze mirrors as reproduced below:

Cu 68.05%, Sn 21.70%, Pb: 3.53% for mirrors dated to the Warring States;

Cu 67.14%, Sn 24.14%, Pb 5.43% for mirror dated to the early Han;

Cu 67.07%, Sn 25.42%, Pb 4.47%, Zn up to 6.73% for mirrors dated to Han dynasty;

Cu 69.03%, Sn 24.62%, Pb 4.68% for mirrors dated to late Han;

Cu 66.68%, Sn 9.75%, Pb 18.99%, Zn 8.24% for mirrors dated to Song-Jin dynasty.

In all cases the copper fraction remains remarkably consistent while the tin and lead fractions also remain very similar until the late Han. No quantitative error estimation or sigma dispersion on these averages have been provided, despite the precise percentages reported. The varying zinc fractions found in mirrors from the Han and Song-Jin dynasties likely reflect contamination by this element in the base ores used and available at these times. Zinc has a much lower melting point than copper and even in ancient times was likely expelled as a gas during the bronze smelting process. It was not smelted in China as a metal until the middle of the 16th century [8]. High levels of zinc (> 10%) in a mirror would therefore indicate a modern reproduction or forgery.

Kong et al. [9] also showed that a copper/tin ratio found for 8 mirrors dated to the Warring States was 3:1, consistent with the table from [7] that is partially reproduced above. Modern research also reveals the copper/tin ratios found in Chinese mirrors is typically close to 3:1 [10–12]. The high tin content compared to other typical bronze objects (such as sacrificial cooking vessels and ornaments) yields an alloy that is hard and brittle. However, it can provide a nice silvery-white colour and is suited to enabling a very good polish and hence an excellent reflective surface for a mirror.

Mirror finishes

Bronze mirrors were polished after casting to make the surface as smooth as possible to render the best reflective property. Unlike other bronze objects the mirror has a specific and special function so the reflective surface has to be treated to increase the reflective effectiveness. Before the Song dynasty, Xiuwu xun in Huainanzi, 淮南子[13] mentions that quicksilver was applied to the surface of the mirror and polished in by rubbing with white felt. Quicksilver is a mixture of tin and mercury paste. This process is also called xuan xi 旋洗. Later historic records by Tiangong Kaiwu 天工开物 (Ming dynasty by Song Yingxing) [14] described a similar polishing technique. It was in the Ming dynasty that the combination of mirror manufacturing and associated cultural flourishing led to an accompanying commercial business for maintaining the reflective surfaces of mirrors in a good state.

High tin bronze patina

Just like other archaeological bronzes, excavated Chinese bronze mirrors present diverse patinas and corrosion products. These depend on the drainage and condition of the burial region and patination process as the soil mineralogical constituents and water content have a very significant effect on the bronze. The exact constituents of the copper alloy and manufacturing finishes also affect the corrosion process. However, in many cases, bronze mirrors have a tin-rich surface due to the final treatment by the so-called “xuan xi” technique previously described. In these circumstances the mirror surface will be

oxidized to varying degrees and react with the underground burial environment and this can form an anti-corrosion layer. This is commonly called qi gu 锈 and results in a dark black or deep green surface colour and a typically shiny patina. In more modern times there has been much analytical interest in such Chinese mirrors whose surface patina appears very dark or even black as is the case for Mirror 2 in this study in particular. It is generally agreed that the surfaces of these “black” mirrors are no longer metallic but are composed of tin oxides. These result in a ‘tin’ enriched surface together with significant copper depletion compared to the copper fraction in the main alloy (see later for mirror 3).

Introduction to the four mirrors

The four mirrors presented together in Fig. 1a&b. are all round in shape and each has a central ring-knob that allows the mirror to be suspended on a cord or for a rod to be inserted. Based on style and design, mirror 1, with the feather hook pattern (see later), and mirror 2 with a coiling dragons, panchi pattern are nominally dated to the Warring States period (475-221BC). Mirror 3 is significantly smaller than the others and has a very rare jade, patterned annular ring attached to the back surface and is dated to the Han dynasty (202BC-220AD). Mirror 4 is the most corroded but is also unadorned and simple without any cast pattern. It is likely a shamanistic mirror and dated to the Song dynasty (960–1279). The iconography and design of these four mirrors are fully compatible with the estimated time periods of their potential manufacture.

The basic physical characteristics of these 4 mirrors are given in the Table 1 below. The observed variation in thickness is due to the variable corrosion across the surfaces.

Table 1
Physical properties of 4 mirrors

Mirror #	Mirror 1	Mirror 2	Mirror 3	Mirror 4
Period	Warring States	Warring States	Han	Song
Diameter/mm	85	97	59	84
Weight/gms	73.98	103.1	35.0	121.0
Thickness/mm	1.97–2.15	1.56	1.99–2.02	3.3

Scientific Investigations Of The Four Mirrors

Investigations into the physical characteristics of the 4 mirrors were undertaken using the following instruments and equipment housed within the ACLab at the University of Hong Kong.

Microscopic examination

A standard binocular microscope and an Olympus S2 × 10 binocular microscope with U-TV1X-2 adapter and attached digital camera and a “Nikon Eclipse LV100N Pol” polarized light microscope (PLM) with NIS-Elements and with” D5.00.00” 64-bit software were used to observe and record the microscopic morphology of manufacturing marks, corrosion and archaeological evidence on all four mirrors. An 1000X endoscope was also used for high magnification imagery.

UV examination

Ultraviolet light, as provided by a Inova X5MT-WUVT lamp with 365–400 nm wavelength emission, was used to illuminate the mirrors. Any resultant UV fluorescence can help detect any organic residues, resins or adhesives or modern restoration evident on any of the mirrors.

X-ray fluorescence spectroscopy

A Bruker® Tracer IV portable X-ray fluorescence spectroscope (pXRF) was used to provide surface elemental composition via spot testing. On each side of each mirror, no less than 3 spots were tested. Bruker Artex software was used to analyse the resultant data. It is important to appreciate that due to the thickness of the surface corrosion products and the low surface penetration of the pXRF, the base alloy composition for each mirror is essentially unknown.

Results

Results from our investigation into the physical characteristics and remaining trace evidence of manufacture, treatment, corrosion and archaeology are presented below.

Tool Marks

On mirrors 1,2 and 3, polishing marks were seen on both sides. On mirror 1 and 2, by using the polarized light microscope (PLM) with reflected light, parallel lines with sharp angles were observed. This type of line is likely caused by mechanical polishing of the surface. For mirror 1 the marks can be seen on-top of some protruding corrosion products rather than passing beneath them (Fig. 2a & 2d). This indicates that this polishing was done post formation of these corrosion products and that an aggressive cleaning of the surface was undertaken quite recently, perhaps to remove significant corrosion to get to the base metal surface in attempts to improve the mirror “aesthetics”. For mirror 2 it is clear that newer corrosion components have formed on top of some of the presumably older tool marks (see arrowed examples in the figure) while the surface has some inclusions that are many times (10X) larger than those small surface defects seen on mirror 1 (Fig. 2b&2e). Mirror 3 is similar to mirror 2 but has a factor of 3-5x more surface defects with a mixture of broader and finer tool marks. In some cases the cleaning tracks can be seen going through these surface defects. In another case (top left of Fig. 2c) these tracks are under the corrosion. These tracks also have a broader spread of angles across the surface indicating several different cleaning episodes. Due to the highly corroded surface, there is no polishing marks able to be observed on mirror 4.

Patina

Mirrors 1 and 2 have a black, shiny patina on their fronts (see Fig. 1b) common to mirrors from the Warring States period. The areas without corrosion still present a reasonably reflective surface. Mirror 3 has as a variable, very dark to lighter green patina. From a region towards the edge of mirror 3 where the overlaying shiny patina has become detached, the division of surface patina and further corroded metal underneath is distinctive. In this small area, where the lighter shiny olive green patina has come away, a lower level “crinkly” sub-surface is evident Fig. 3 (left). This is seen in many other bronzes from antiquity. An example is shown in Fig. 3 (right) of a 2nd century AD Roman brooch from Cirencester museum in the UK (photo taken by the 2nd author in-situ in December 2017). This is shown next to mirror 3 together with arrowed inserts showing the common patination features. Both mirror and brooch are from approximately the same time period, both are small in size and have similar light to dark olive green shiny patinas. However, in both examples the top level patina has flaked off in some places to reveal a crinkly, sub-surface condition. Such features are, to our knowledge, not present in modern replicas.

Remaining Archaeological evidence

Mirror 1 does not have any obvious archaeological evidence such as any encrusted earth deposits or any other phenomenon related to a burial history such as attached organic material, including textile pseudomorph marks from wrapping in cloth prior to burial. Mirror 2 does have some apparent encrustation remaining on the mirrors’ 3 mm wide edge that extends for about 2 cm. Images of this attached encrustation are shown in Fig. 4a&b at 40x and 1000x magnification respectively. A fine implement can remove this material quite easily. Both mirrors 1 and 2 appear to have been heavily cleaned (see Figs. 2a-b). For mirror 3, within the incisions of the inscribed pattern of the jade annular attachment, some traces of earthen encrustations were also observed. By touching by scalpel, these encrustations are very hard to remove (Fig. 4b). It looks natural. The formation of this type of crust on a jade surface is usually caused by a prolonged burial history. The jade annulus itself is 12 mm wide with an outer diameter of 52 mm and inner diameter of 28 mm with a typical late-Warring States simple, scroll-type, panchi pattern. From microscopic examination, it is clear this piece was not worked with modern machine tools but betrays the tell-tale marks and scratches typical for jade hand-worked from this period and evident in Fig. 4c. The jade annulus itself is possibly at least partially recessed into the bronze mirror being almost flush with the surface on one side with a protruding thickness of ~ 1.9 mm for the most part but closer to 3 mm for the inner edge closer to the central boss.

On mirror 4, the overall surfaces are quite heavily corroded and covered with deep greenish blue corrosion products raised from the base mirror surface together with some white crust along one edge. Textile pseudomorph marks were observed on this particular corrosion layer (see Fig. 5a,b). This area also fluoresces bright yellow under UV light indicating some organic material is present in this region (see Fig. 13) The impressed textile marks look natural. From the woven pattern (Fig. 5b), it is likely from a linen fabric. It is not rare to see such textile pseudomorph marks on bronze mirrors and other bronzes. As an important and elegant personal belonging, mirrors were usually buried with the owner, and sometimes

wrapped with a textile [15, Fig. 10]. After a long time underground, the textile, which is an organic material, deteriorates away to nothing and only residual marks can be left on the surface corrosion, especially in the regions where underground water levels fluctuate actively. Several insect carcasses can also be seen embedded in the thick corrosion (see Fig. 6).

Corrosion morphology

The surfaces of mirror 1 have been well preserved but extensive abrasive cleaning seems also to have been undertaken perhaps in the recent past. On the front surface, towards the mirror edges severe pitted corrosion can be seen in several places that has eaten into the smooth, light green surface patina. By looking at these areas where the surface patina has been broken-up, 3 distinct layers can be distinguished (see Fig. 7). The top layer is a light green shiny patina, underneath is a black layer and under this is a layer of greenish powdery, pitted depressions. It is hard to tell if the corrosion starts from inside the metal or has ingressed from outside. We believe the black middle layer is the original mirror surface akin to what is seen for mirror 2 and resulting from application of the “xuan xi” technique referred to earlier.

However, given the absence of metal surface where the pits are exposed and the trend of the increasing density of number of pits around the powdery area, it is very likely that the corrosion starts from each single pit where moisture has gotten into the metal to stimulate the process of decuprification to form green corrosion and then turn into powdered corrosion. In certain regions the original metal surface is gradually replaced by this green corrosion. Along with forming increasing green powder corrosion, the green surface has been eaten away. Therefore, the green surface is the middle phase of the whole deterioration process. On the back surface, towards the mirror edges, the green layer is absent where a black rough metal underneath is exposed (Fig. 8).

For mirror 2 both front and back surfaces are very well preserved with the surfaces very dark, almost black in colour. However, a similar corrosion phenomenon (Fig. 9) to mirror 1 can also be seen on parts of the front surface of mirror 2 although in this case there is no additional green surface patina on top of the dark layer. It is possible this has been removed by aggressive cleaning. Both mirrors one and two were acquired at the same time from the same vendor. On the back surface towards the edge in one area in particular, a rougher surface is observed. It was likely formed during the manufacturing process since part of the relief is disturbed (Fig. 10).

For mirror 3 the front surface is mainly smooth and dark. However, there are regions of bright green malachite corrosion along with small regions of red corrosion which is assumed to be cuprite, as shown in Fig. 11. The corrosion looks natural. On the front surface there is also a meandering hairline crack within the body of the mirror (refer Fig. 14) that does not extend to the edges. It has an overall extent of ~ 5 cm.

Mirror 4 is covered with thick green corrosion products. In some regions, small, black “charcoal” like inclusions can be seen within the corrosion (Fig. 12 right). The overall corrosion looks natural.

UV fluorescence Imaging

UV fluorescence imaging has been a valuable diagnostic tool in the art and archaeology fields since the 1920s [16]. Four mirrors were subjected to UV illumination to detect if any modern restorations, e.g. using adhesive/paint to reattach surface patina, have been done. For Mirror 3 and 4, due to the potential surface organic archaeological evidence remaining, observation was also carried out on these specific targeted areas. The results show that no restorations have been found on all mirrors. Mirror 3 had evidence for a brown “glue” under the jade annulus that is fixing it onto the back surface of the mirror. UV imagery did not reveal any fluorescence indicating that whatever was used to fix the jade annulus in place was not any modern resin or adhesive. Furthermore, the strongly attached encrustations here and there within the jade carvings did not fluoresce either so are not modern glued-on material sometimes used to create an impression of authenticity by the unscrupulous. However, UV imagery of Mirror 4 did reveal in stark relief the grey-white areas of corrosion associated with the textile pseudomorph regions. This indicates that organic components may remain in the fluorescent region.

Surface Metallurgy from pXRF measurements

For each mirror, 3–4 test spots were chosen for analysis using pXRF. Here it is crucial to appreciate that the pXRF measurements only penetrate a small distance into the surface. Hence, where the corrosion is thick, only these products can be assessed. All data was therefore from the surface but the cleanest regions where chosen wherever possible. For mirror 4, the data was collected from the area where with less green corrosion. The “vacuum” attachment and lower kV and high current was used for the corroded area in order to detect chloride and lighter elements. Bruker® Artax analytical software was used to analyse the data. By analysing the net count rates, which are the number of photons recorded for each element after removing other elemental interference and background, a percentage by abundance for each recognized element was calculated. Given the data was taken from the surface layers, where any corrosion or residues would affect the absolute value, the results should be regarded as semi-quantitative only. Table 2 indicates average percentage of major elements on the surfaces of each mirror from the combined 4 spot measurements. The blanks mean that the listed element was not detected at the low abundance limit of the instrument.

Mirror 1	Cu K12	Sn K12	Sn L1	Pb L1	Pb M1	Hg L1	Hg M1	Fe K12	Zn K12		Cr K12		
Reflective front average	69%	17%	1%	8%	0%	0%	0%	0%	1%		0%		
Knobside average	60.93%	20.68%	1.55%	11.20%	0.02%	0.02%	0.02%	0.58%	0.67%		0.12%		
Mirror 2	Cu K12	Sn K12	Sn L1	Pb L1	Pb M1			Fe K12	Zn K12		Cr K12		
Reflective front average	47.81%	24.10%	1.48%	20.20%	0.11%			0.12%	2.06%		0.60%		
Knobside average	54.37%	22.39%	1.52%	15.70%	0.06%			0.35%	1.36%		0.36%		
Mirror 3	Cu K12	Sn K12	Sn L1	Pb L1	Pb M1	Hg L1	Hg M1	Fe K12	Zn K12	Ca K12		Mn K12	Ni K12
Reflective front average	19.68%	50.73%	2.65%	14.71%	0.00%	0.77%	0.06%	3.57%	0.12%	0.85%		0.01%	0.03%
Knobside average	11.78%	50.89%	1.96%	10.40%	0.00%	0.40%	0.04%	4.63%	0.45%	2.49%		0.18%	0.02%
Mirror 4	Cu K12	Sn K12	Sn L1	Pb L1	Pb M1	Hg L1	Hg M1	Fe K12	Zn K12				
Reflective front average	49.91%	2.38%	0.13%	37.64%	0.26%	1.11%	0.02%	0.27%	0.58%				
Knobside average	72.67%	1.03%	0.01%	22.08%	0.10%	0.09%	0.01%	0.12%	0.38%				

Table 2
Copper
alloy of
four
mirrors
from
pXRF
analysis

Note

Recorded percentages of the rare earth metals Pd, Rh and Ru are from the pXRF instrument itself and so are not included in the Table 1 but help explain why the totals do not add up to 100%.

Data was at 40 kV, 20 μ mA, yellow filter for metal analysis, 120 second exposure for each spot. The results are the averages from the 3–4 spot measurements. The K12, L1 and M1 designations refer to electron shells where K denotes the first shell (or energy level), L the second shell and M, the third shell.

The four mirrors are all bronze, i.e. a copper-tin-lead ternary alloy. However, the ratios vary markedly. Zinc is not over 10% in any of these mirrors which indicates that none are poorly made and easily acquired modern fakes where high levels of zinc are common [17, 18].

The Cu-Sn ratios on surface in Mirror 1 fall within recorded common ranges as around 3:1, Mirror 2 is about 2:1. As for lead fraction, according to Wang [19], lead on the surface of mirrors dated to the Warring States ranges from 9.35–12.83%. The 20.20% lead value measured for Mirror 2 is much higher than the reference record. Furthermore, the range in the amounts of tin and lead found in mirrors 1 and 2 does not match the opinion of He [20,p. 76] who states that mirrors dated to the Warring States in most cases have a tin fraction that is much higher than lead. Here it is only 17–24% tin c.f. 8–20% lead. He [20] also indicated that the mirror dated to the Warring States with low fraction of iron (Fe) were probably unearthed from central china Shaanxi, Shanxi province or from inner Mongolia.

For mirror 3 the surface copper content is extremely low while the tin content is 50%. The likely applied “xuan xi” surface treatment would contribute to this outcome. Although this data was achieved from surface measurements, the presence of a crack indicates the brittleness of the alloy on this mirror (Fig. 14). Similar data on Cu-Sn ratios was achieved on mirror surfaces by He [20] and given in a scientific report [21] by the lab in University of Science and Technology of China in 1988. The drawback of high tin is that it can lead to a brittle copper alloy. Indeed on mirror 3, a crack on the reflective front has already been noticed (see Fig. 14). Most published data [11, 12, 20–22] on the lead content on the surface of mirrors dated to the Han dynasty are less than 10%. Wang (1995) gave a wider range of 7.27–20.4%. Therefore, the lead in mirror 3 is actually in the reasonable range for provenanced Han bronze mirrors.

For mirror 4, the Cu-Sn ratios are far from 3:1. Other archaeologically provenanced mirrors dated to the Song dynasty with high lead content have also been reported. According to He & Song [20], a Song mirror unearthed from Linxi, Shandong province (northern China) presents a high lead content (35.11–35.75%) on its surfaces. Conversely, mirrors unearthed from Echeng City in Hubei province (southern China) show a relatively low lead component (average 20.220% for 12 mirrors) [24]. An interesting phenomenon for mirror 4 is the much more highly corroded surface compared to the other three mirrors and that the measured lead fraction is high, averaging ~38% on the front surface. There are two possible explanations and sources for the lead. 1). It is migration to the surface from within the alloy itself; 2). It arises from the lead mercury finishing paste used to keep the reflective surface shiny [20]. This could at least also partially explain why the front surfaces for mirrors 2, 3 and 4 also have a higher lead content. No matter what the source is, lead is an active factor in causing more corrosion. This is also true for other types of bona-fide archaeologically excavated bronzes with high lead content [23]. The known process of the migration of lead within the alloy also affects the composition of the distinct but localised white crust that bears the textile marks (pseudomorphs) on mirror 4. The pXRF result shows that this crust on mirror 4 has a very high lead value (Pb L1 50.28%, Pb M1 0.41%).

Presence of mercury (Hg)

Trace but reliable levels of mercury (Hg) were detected on both mirrors 3&4, indicating that these two mirrors at least were likely treated with the quicksilver polishing technique described in the historical records. The nominal low level detection of Hg on the decorated reverse side of mirror 1, though not considered reliable, is interesting and could also indicate past such treatment where aggressive cleaning of the reflective surface has removed almost all traces of mercury on that side. No mercury was detected on mirror 2. It is hard to conclude that no mercury was used to treat the mirrors since if heat was involved during the process, the mercury may evaporate [25].

pXRF of the corroded areas

The pXRF with settings of 15Kev, 36 μ A, vacuum implemented and with 120 second exposure testing times were used to analyse chosen corroded areas on pitted areas of mirror 1 and 2 to detect chloride (Cl) which commonly causes ‘bronze disease’, seen as greenish white powder on bronzes [26]. However, no chloride was detected. For mirror 3, data was collected on the green corrosion on the reflective surface as

in Fig. 11. Green corrosion and earthen crust on mirror 4 were also analysed. Chart 1 shows the elemental distribution on the targeted areas on four mirrors.

Presence of chromium (Cr)

There is chromium (Cr) present on both mirrors 1 and 2 as a trace element. A few ancient bronzes have been discovered bearing chromium that have been studied in the past 30 years. Scholars are interested in whether such chromium was added deliberately by the ancients for anti-rust purposes. However, most investigations [27–29] pointed out that the chromium was not an intentional addition but a contamination from the natural environment, except perhaps for one bronze Pan dated to the Warring States Chu Culture[30]. The content of chromium in the sample surface-film by Luo [30] for this bronze Pan is 35.61%, much higher than the average content in any other publication and much higher than found here for mirrors 1 and 2 (less than 1% chromium). As chromium(III) oxide (Cr_2O_3) is a modern polishing product used on metal we conclude that the detected chromium is more likely a result of cleaning with chromium oxide more recently, especially considering the sharp angled modern polishing tool marks observed on the reflective surfaces on mirrors 1 and 2. Interestingly, these two mirrors came from the same dealer. This may also explain the absence or very low levels of mercury on those two mirrors, where a heavy, abrasive polish could have removed any remaining trace mercury.

Discussion And Conclusions

Four Chinese bronze mirrors from a private collection and dated to the Warring States (mirrors 1 & 2), Han (mirror 3) and Song (mirror 4) dynasties have been assessed. Close examination and scientific surface investigation and application of various forensic testing processes was employed. Different microscopic corrosion morphology and features, including archaeological, have been noted. The wide differentiation in corrosion characteristics evident are likely caused by the strong variations in bronze alloy composition found from surface pXRF, together with their burial histories and subsequent cleaning, handling and curation treatments each has been subjected to.

Mirrors 1 and 2 share certain common features and both have black patinas, particularly extensive on mirror 2. This is quite a common feature for mirrors of the Warring States period. They also both have surface pitting as well as residual corrosion. It is possible much of the original corrosion has been removed by strong abrasive cleaning as evidenced by the surface scratches seen on the shiny green patina remaining in places on Mirror 1 and the chromium oxide residue found on both of these mirrors that in itself could have created some of the surface pitting seen. Unfortunately, no photomicrographs on similar corrosion phenomenon on archaeological mirrors has been published which could help to figure out the feature of natural occurred pitting or if it is caused by a corrosive agent. Since these two mirrors were reportedly acquired from the same vendor and likely treated before acquisition by the current owner in attempts to render them more aesthetically appealing, the original trigger of the remaining visible corrosion remains unknown. The corrosion on mirrors 3 and 4 while very different looks natural and authentic and in both cases there is residual archaeology.

The observed Cu-Sn-Pb ratios revealed by pXRF for mirrors 1, 3 and 4 fall into the range of published data from archaeologically excavated and provenanced mirrors. This is not the case for mirror 2 which has an unusually high lead content.

In summary, the designs, patination, corrosion and metallurgy of mirrors 1, 3 and 4 are consistent with that expected for genuine artifacts and this is re-inforced in particular by residual archaeological evidence for mirrors 3 and 4. A firm assessment for mirror 2 is currently not possible as questions as to the cause of rough surface on back side and its high lead content remain. Although mirror 1 was collected at the same time as mirror 2, and both of them were probably polished in modern time with Cr_2O_3 , we nevertheless believe its green surface patina fused with a black surface around pitted areas cannot be easily created in a short time frame but usually takes centuries. Mirror 3 has trace archaeological evidence of a burial history due to the residual encrustations on the jade insert. Such jade inserts on bronze mirrors are exceptionally rare with only a few examples known. One example can be seen in the collection of the Fogg Art Museum, Harvard University, in *Hai-Wai Yi-Chen: Chinese Art in Overseas Collections, Bronze I* [31, p. 171]. It is also possible that the jade annulus was added later as its iconography is typically of the warring states and so it is possible this is an older jade of this common *bi*-disk form that had a mirror made specifically for it in the Han period given the mirror itself is unusually small. Jade is extremely durable and was passed down and re-used in antiquity. Mirror 4 is dated to the Song dynasty and also has multiple, interesting archaeological trace evidence including textile pseudomorphs, insect shells and incorporated “charcoal” inclusions. It was perhaps unearthed in northern China and its antiquity is also assured.

Declaration

Availability of data and materials

The dataset generated from this study is stored in the ACLab and available from the corresponding author on reasonable request.

Declaration of competing interest

The authors declare that there are no known conflicts of interest associate with this publication and there has been no significant financial support for this work that could have influenced its outcome.

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Author's contributions

Tests and data interpretation were carried out mainly the first author and evaluations mainly by the second author.

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Abbreviations

UV

Ultraviolet

pXRF

portable X-ray florescence spectroscopy

PLM

Polarized light microscopy

Declarations

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Figures

Figure 1

The back surfaces of the four mirrors placed alongside each other in the same ambient, natural light with ID number as used throughout and a ruler for the physical scale.

Figure 2

The front surfaces of the four mirrors

Figure 3

Surface tool marks (scratches) on Mirror 1. It can be seen that these marks go across corrosion products on the mirror surface and are not beneath this corrosion. This indicates later abrasive cleaning of the reflective surface of this mirror.

Figure 4

Polishing lines (scratches) on reflective surface of Mirror 2. Some of these have sudden sharp angled changes in polishing lines likely due to some mechanical polishing process. Here some corrosion products sit on top of some of these marks indicating an older polishing process.

Figure 5

Polishing lines on reflective surface of Mirror 3. There are a mixture of fine and broad parallel streaks indicating different cleaning abrasives and likely different periods of cleaning. There are a larger number of surface defects per unit area compared to mirrors 1 & 2.

Figure 6

40x image of region of top-level thick (~200micron) green patina on the back surface of mirror 1. Evidence of strong abrasive cleaning is seen as parallel score marks on this green patina. The more corrugated metal underneath where this patina has become detached is also clear.

Figure 7

40x image of part of the shiny, black patina on the back surface of mirror 2 taken on one of the spiral patterns. Again, very clear evidence of strong abrasive cleaning is seen as a series of fine criss-crossing

linear score marks. The fine shine on this side likely indicates recent abrasive cleaning.

Figure 8

Montage of Han mirror 3 (left) and 2nd century AD roman brooch (right) with inserts highlighting the common patination feature.

Figure 9

40x image of residual encrustation on the edge of mirror 2. The feature extends for ~2cm along the edge of the mirror and has a dark brown-grey color but lighter at the exposed edges.

Figure 10

1000x image of this encrusted area that is seen to be composed of a sandy conglomerate of fine particles 10-100microns in size.

Figure 11

Earthen crust deposit in the incisions made on the jade ring annulus attached to the back of Mirror 3. The scale to the right is in mm.

Figure 12

White region of mirror 4 back surface showing textile pseudomorph impressions left by a linen type fabric used to wrap the object during burial. The pitch between warp and weft is $\sim 0.5\text{mm}$. The scale to the right is in mm.

Figure 13

40x close up of textile pseudomorph for mirror 4 – the character of the decayed woven material is beautifully preserved.

Figure 14

Several insect husks ~1mm in size embedded into the heavy corrosion products on the back surface of mirror 4. The scale to the right is in mm.

Figure 15

Region at the edge of the back surface of Mirror 1 showing the top layer (shiny green patina), middle black layer and pitted, powdery corrosion underneath. The scale to the left is in mm.

Figure 16

Reverse surface of mirror 1 showing regions of the top smooth, green patina that is largely flaked off to reveal the black, metal layer underneath, there is little pitted corrosion in this region.

Figure 17

Pitted corrosion on the front surface of Mirror 2. The scale to the right is in mm.

Figure 18

Close up of the coiled dragon pattern on the black back surface of Mirror 2 showing an area of dark surface encrustation towards the edge. The pattern definition looks sharp and clean until this point.

Figure 19

Green malachite and red cuprite corrosion near the centre of mirror's 3 reflective surface.

Figure 20

Complex uplifted corrosion products on the surface of mirror 4 (left) and some black inclusions 1~mm in size in the same surface located towards the mirror's edge. The scale in the image is in mm.

Figure 21

UV imagery of back and front surface of Mirror 4. The lighter areas correspond mainly to the textile pseudomorph impressions.

Figure 22

40X Magnified region of the crack on the reflective surface of Mirror 3.

Figure 23

shows the elemental variation on the corroded area of these four mirrors. The pitted areas on mirror 1 and 2 are found to be mainly copper and tin compounds, no chloride was detected. Chromium is only present on mirrors 1 and 2. Lead dominates the earthen crust on mirror 4.