EARLY CHINESE BLACK MIRRORS AND PATTERN-ETCHED WEAPONS

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INTRODUCTION

Among the bronze mirrors produced in China during the Chou and Han periods, some exhibit shiny black surfaces. Black shiny surface finish is not uncommon among Chinese mirrors, but also not universal; some of the mirrors recently discovered in controlled archaeological excavations in the People's Republic of China have the characteristic black appearance; others do not. In some instances both black and non-black mirrors have been found in the same tomb and burial environment.

Mirrors with the shiny black surface are unusually corrosion-resistant. When corrosion occurs, it does so in a very typical manner; the surface of the object is not attacked uniformly. It appears to crack or splinter locally and corrosion occurs from underneath. The corrosion products form small and isolated pockets within the still unattacked original surface. They look like warts or chicken pox; every observer emphasizes this phenomenon. The blisters contain the normal green copper salts that one finds on corroding bronzes. Frequently, as corrosion proceeds, it lifts the shiny surface above the corrosion products.

Black mirrors share other common characteristics; they show a glossy, often jet-black (sometimes dark green or brown) surface on the face of the mirror and on undecorated areas of the back. Usually the black is shiny, with a vitreous luster. The relief-decorated portion of the back is also black, but it appears dull. The loop in the center of the back is evenly black, both on its top and underside. The mirror back underneath the loop is black as well. Visual inspection of the decorated back reveals no discontinuities of the black surface within the ornamentation, although relief decor can be quite deep and complex. On the plain face one can often detect polishing marks *under* the shiny surface layer.

Mirrors with the shiny black surface are not limited to one particular style or period. Most of the known late Chou mirror types can be found with the black surface. Black mirrors range in date from Middle Chou through Han to T'ang,[1] although we are not sure that all the dark finishes found on mirrors, especially the post-Han mirrors, are of the same chemical and mechanical nature as on the earlier material. Furthermore, the characteristic black surface is not restricted to mirrors: some weapons and utensils also show similar glossy, dark and highly corrosion-resistant surfaces.

Is this special surface the accidental result of environmental conditions, or is it an intentional surface finish, purposely produced by the ancient craftsmen? If it is a natural corrosion product, is its special color and chemical inactivity due to some inherent

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[1] See below, section entitled "Geographical and Chronological Limits of Black Mirrors."

property of the metal, or solely to environmental conditions?

If it is, on the other hand, an intentional surface finish, is it the result of special casting conditions and/or metal composition, or is it a post-manufacture, or possibly a post-use, process? How was it produced? What were the reasons for the special surface finish?

BLACK-SURFACED MIRRORS

PREVIOUS INVESTIGATIONS

By providing technical details on the structure and composition of the ancient objects, a number of investigators have attempted to answer the above questions. In this century, the first study in English was that by Orvar Karlbeck in 1926. His article simply stated, "Some specimens are coated with black or brown lacquer and others show traces of beaten gold."[2] Since then, the "black lacquer" designation has been applied often to characterize certain mirrors; no one has yet put forward technical evidence for the presence of lacquer; its absence has, however, been specifically reported.[3]

One exception to this statement is the recent study by Bulling and Drew.[4] While not specifically concerned with *black* mirrors, the authors report the presence of dark lacquers that they consider as being applied well after the manufacture and use of the mirrors; however they provided no experimental evidence.[5]

In 1931, Yetts addressed the question of the black bronze mirrors quite specifically.[6] He expressed strong criticism of Collins' just-published paper on corrosion of early Chinese bronzes.[7] Collins stated his opinion that the black mirror surfaces had obtained their particular properties as a consequence of special environmental factors. He considered the black surface to be a natural patination resulting in a very stable form of cuprite of unknown morphology. To this, Yetts replied:

> I have long held the view that the quality of this coating is so perfect and uniform that the generally accepted explanation of a patina due to accidental changes of environment fails to carry conviction. At my request, Dr. H. J. Plenderleith has been good enough to make a chemical examination and he finds that the black coating withstands all reagents except a mixture of nitric and hydrofluoric acids. This fact suggests the possibility that the coating may have been intentionally produced by

[2] Orvar Karlbeck, "Notes on Some Early Chinese Mirrors," *The China Journal of Science and Arts*, vol. 4, no. 1 (1926), pp. 3–9.

[3] Rutherford J. Gettens, "Some Observations Concerning the Lustrous Surface on Ancient Eastern Bronze Mirrors," *Technical Studies in the Field of Fine Arts*, vol. 3 (1934), pp. 29–37; *idem*, "Tin-oxide Patina of Ancient High-tin Bronze," *The Bulletin of the Fogg Museum of Art*, vol. 11, no. 1 (1949), pp. 16–26; see esp. p. 19.

[4] A. Gutkind Bulling and Isabella Drew, "The Dating of Chinese Bronze Mirrors," *Archives of Asian Art*, vol. 25 (1971–1972), p. 38; *MASCA Newsletter*, vol. 7, no. 1 (June, 1971), pp. 2–3.

[5] One of the authors (WTC), while examining Chinese bronze mirrors in the storage of the Field Museum, Chicago, in 1977, found one that appeared to be lacquered. The coating was thick and brownish, it looked quite different from the black-surfaced mirrors in the same drawer. The object was not sampled or analyzed, however.

[6] W. Perceval Yetts, "Problems of Chinese Bronzes," *Journal of the Royal Central Asian Society*, vol. 18, part 3. (August 1931), pp. 399–402.

[7] William F. Collins, "The Corrosion of Early Chinese Bronzes," *Journal of the Institute of Metals*, vol. 45 (1931), pp. 23–55.

> mixing siliceous matter with the layer of the mold which comes into direct contact with the molten metal. Thus, a coating of a compound somewhat like silicon bronze may be produced. The problem must be investigated further before any definite statement can be made.

Unfortunately, neither Yetts nor Plenderleith himself did provide further details. Plenderleith simply stated that he detected silica in amounts large enough to convince him that it was intentionally introduced, but he did not elaborate on how the color and properties of the mirrors could be related to the presence of SiO_2.[8]

In 1934, both Collins[9] and Gettens[10] gave the black mirrors more detailed attention. Their papers, appearing almost simultaneously and apparently independently, are the first technical studies of the black bronze surfaces. While Gettens restricted himself to mirrors, Collins analyzed, in addition to mirrors, a sword fragment and a Korean bronze bowl. Gettens' interest in mirrors had been aroused initially by the objects in the Hoyt Collection at the Fogg Art Museum; later he was to obtain access to the mirrors of the James Marshall Plumer collection, which allowed him to broaden significantly his experimental base.

Collins was a mining engineer, not a professional sinologist; in addition to including analyses from the Japanese literature, he used objects that he had collected in China.[11] While Gettens kept reprints and excerpts from Collins' papers and quoted Collins in publication, there is no evidence that the two ever met or corresponded. One cannot help speculating on what would have happened if these two men had had an opportunity for collaboration. Their work is strikingly similar.

Both were basically experimentalists, doing their own microscopy and chemical analyses. Collins used the laboratories at the British Museum and at Imperial College; Gettens used those at the Fogg Art Museum and the Harvard University Chemistry Department. Both pointed to the characteristic corrosion on the mirrors, both reported the absence of mercury and organic materials. Their chemical analyses agreed: both reported mirror bronze composition around 70–75% copper, 20–25% tin, 1–5% lead. Both documented the inertness of the mirrors' surfaces to chemical attack by cold acids and alkaline solutions, and both illustrated metallographic cross sections in which the surface layers exhibited continuous and gradual transition into the body of the metal.

Collins stated very clearly that it was the α-phase of the alloy that was altered at and below the surface. In addition to the examination of cross sections, he also examined a mirror normally to the black surface; first in its original condition, and then after each increment of polishing down the surface until the unaltered bronze was reached. He observed that the surface material completely lacked any discernible grain structure and

[8] Harold J. Plenderleith, "Technical Notes on Chinese Bronzes with Special Reference to Patina and Incrustation," *Transactions of the Oriental Ceramic Society*, vol. 6 (1938–1939), pp. 33–55.

[9] William F. Collins, "The Mirror-black and 'Quicksilver' Patinas of Certain Chinese Bronzes," *Journal of the Royal Anthropological Society of Great Britain and Ireland*, vol. 64 (1934), pp. 69–79.

[10] Gettens, "Some Observations . . ."

[11] In his 1931 paper on corrosion, read at the Institute of Metals by C. H. Desch in the author's absence, Collins was identified as "Agent in Peking of the Anglo-French China Corporation and S. Pearson and Sons (Contracting Department)."

that the alteration products (which Collins thought to be cuprite) penetrated deeply into the interior of the mirrors. Collins coined the term "rooted" in this context.

Both Gettens and Collins noticed that the mirrors were in the "as-cast" condition, and both saw the presence of redeposited copper in the matrices. In an unconscious parallelity of approach, both men turned to the then novel X-ray diffraction technique for help in the identification of the unknown product on the mirrors' surface.

Here their work diverged. Ironically, both seem to have missed a major point of information. The surface layer of black mirrors is very difficult to remove; the first X-ray diffraction patterns obtained for Gettens by J. Norton at the Massachusetts Institute of Technology showed very weak and diffuse lines that do not appear to correspond to any simple pattern.[12] Later, Gettens dissolved the material removed from the surface by boiling it in concentrated hydrofluoric acid. He found that the residue, which remained after evaporation of the acid, showed the presence of tin in a microchemical test. He does not seem to have tested for any other elements. In 1949 Gettens tried again to obtain X-ray evidence. He reports that:

> Samples weighing about 1 mg were scraped from the smooth surfaces of two mirror fragments and these were leached with 1-to-1 hydrochloric acid to dissolve out copper compounds and any traces of iron that might have got into the sample from abrasion of the sampling tool. After careful washing, the samples were compared microscopically with the untreated samples and they appeared not to have been physically altered by the treatment. X-ray diffraction pictures were then taken.

The X-ray diffraction patterns again showed broad lines, but they could be measured and identified. They corresponded closely or exactly to the patterns of artificially prepared stannic oxide, though not to the pattern of the mineral cassiterite.[13]

Gettens also noticed a difference in the optical properties of the mirrors' surfaces and those of cassiterite. He had found the mirrors' surfaces to be quite homogeneous and measured the refractive index on several of them. It ranged from $n = 1.78$ to $n = 1.81$. Cassiterite, on the other hand, is tetragonal, with $\omega = 1.997$ and $\epsilon = 2.093$.

The evidence of tin oxide led Gettens to believe, from then on, that the unique properties of the black mirrors were due to a special tin oxide patina, a variant of the "water patina" often found on ceremonial bronze vessels. He admitted freely that the color, the subsequent mode of cracking and corrosion attack, as well as the chemical stability of the black surface layers were difficult to explain on this basis.

Collins, on the other hand, had established in his general study of the corrosion of bronzes that the first corrosion product of ancient bronzes was cuprite. This was done for him by X-ray diffraction carried out at the British Museum by F. A. Bannister. Seeing no fundamental difference between the metallographic structure of the black high-tin bronze mirrors and other bronzes of similar composition, and believing that the black surfaces were natural occurrences, Collins found himself faced with the need to reconcile

[12] Gettens, "Some Observations . . ."

[13] Gettens, "Tin-oxide . . .", p. 22

the color and the composition as cuprite. He summarized his conclusions as follows:

> 1. The (mirror-black) patina of certain early Chinese bronzes consists of crystalline cuprite (cuprous oxide, Cu_2O) of unusual mineral structure, possibly having a thin film of tenorite (black cupric oxide, CuO) on its surface. Bronzes bearing this patina are usually of silver-white or nearly white metal, with chemical composition and crystallographic structure closely resembling . . . speculum metal . . . .
> 2. Speculum metal appears to owe its 'rustless' property to its high proportion of fine-grained duplex (alpha plus delta structure). The resistance to corrosion of the cuprite which grows out of it and upon it, may be due to the like structure acquired from its parent alloy. (Under natural conditions, some massive crystals of cuprite alter on their crystal faces to malachite and thus acquire a green 'patina'. Others do not. It is not known exactly why such alterations occur or are arrested.)
> 3. The unusually fine lustre and polished appearance of this patina are due: (a) To original polishing of the bronze . . . (b) To thinness and evenness of the corrosion layer.[14]

This explanation does not at all deal with the fact that there are many Chinese mirrors of the same overall composition which, in fact, have no black surface layers and do not exhibit corrosion-resistant behavior.

Both Gettens and Collins were aware that Plenderleith had found silicon on the black surfaces. But the comment by Yetts—that something like an inert surface layer of silicon bronze could have been produced—may have distracted them from the significance of this information. Gettens pointedly emhasized that "there is no evidence of the formation of any compound like a silicon bronze . . ."[15] If Yetts had not used the term "silicon bronze", which had a much more precise meaning to Gettens and Collins than it may have had to him, then the matter might not have rested here, but it did.

PRESENT INVESTIGATIONS

When, in 1960, one of the present authors (UMF) began to look again at the black mirror problem, it was on the suggestion of the late W. Todd, then chief conservator at the Royal Ontario Museum in Toronto, who was fascinated by the corrosion-resistance of the black bronzes. At that time new experimental techniques such as electron microprobe analysis and X-ray fluorescence made a fresh look at the vexing problem of dark bronze surfaces worthwhile.

The initial samples used were fragments from Han mirrors from the Royal Ontario Museum study collection. Later Gettens put his samples at the disposal of UMF. Basically, the studies included optical investigations and X-ray and electron microprobe studies, as well as determination of density and hardness.

In order to show the nature and results of our investigations we have chosen two examples for this article to illustrate typical "cases." The descriptions on Figure 1 (Mirror #1) and Figure 2 (Mirror #4) come from the catalogue cards in the Royal Ontario Museum. Both figures show the mirrors in present condition, after sampling.

[14] Collins, "The Mirror-black . . .", pp. 77–78

[15] Gettens, "Some Observations . . .", p. 36

FIG. 1.—Mirror # 1, black with patches of bright green; courtesy of the Royal Ontario Museum, Toronto, Canada. The Museum's catalogue card states: 960.234.49; 74 FAE 321; Con # 689/197; Mirror, bronze, round, flat with patches of bright green patina. Hemispherical central knob, square central band with incurving sides, small animal masks inside each corner, main field decorated with four dissolved animal masks and 5 characters of what must have been an 8-character inscription. The whole is surrounded by one inward-facing scallop band and a scroll-pattern border. The Dr. James M. Menzies Collection. Broken in 8 pieces with 3 pieces missing. Late Han. Diameter $6\frac{3}{8}''$ (15.7 cm.)

FIG. 2.—Mirror #4, black; courtesy of the Royal Ontario Museum. The Museum's catalogue card states: 960.234.41; 74 FAE 312; Con #689/195; Mirror, bronze, round with hemispherical knob, surrounded by 12 small circles in relief, enclosed by a broad flattened band in relief. Main decoration in a series of bands, first a band of closely spaced diagonal lines, surrounded by an inscription on a plain ground, a broad flattened band in relief, enclosed by a band of raised closely-spaced diagonal lines, a second inscription, surrounded by another band of raised closely spaced diagonal lines, an unturned flattened rim. The Menzies Collection (Estate of Dr. James Menzies). Broken in 5 pieces. Chinese, Han Dynasty. Diameter $6\frac{1}{8}''$ (15.4 cm).

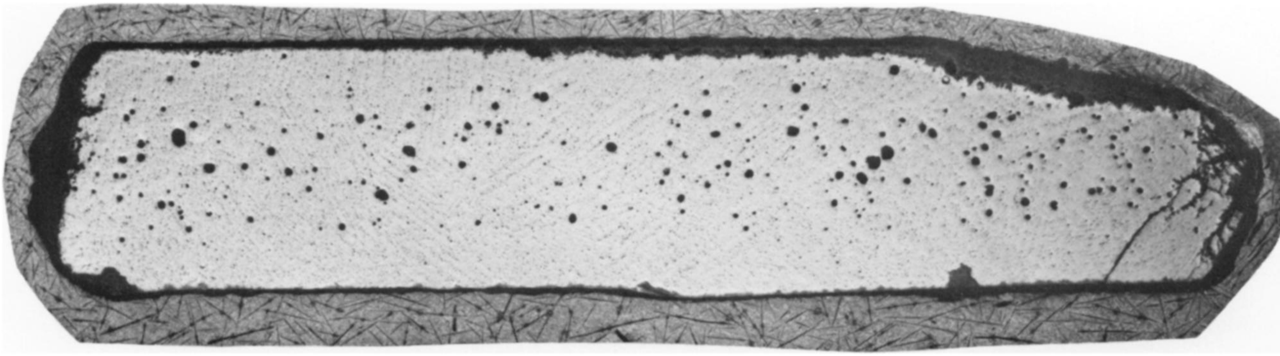


FIG. 3.—Cross section of Mirror #4; mounted in Wood's metal; ×7, bright field, unetched. The section shows the mirror face at bottom and the rim of the back at top; the rim slopes off at the right to the decorated area.

Microscopic studies. Figure 3 shows the fragment from Mirror #4 in full cross section. The fragment, mounted in Wood's metal, is shown in the polished but unetched condition. The as-cast structure and the near-spherical lead particles are clearly discernible. The black surface layer is of uneven thickness. The series of cracks in the narrower side of the fragment are of particular interest. One sees them—usually to a lesser extent—in cross sections of many black mirror fragments. The inside surfaces of the cracks show the same microstructural features as the material below the external surfaces of the mirrors.

Details of a smaller crack are illustrated in Figure 4, in which the external surface is at the top edge of the picture with the crack going at right angles to it into the mirror. It should be stressed that the lead-rich particles (which can be lead or lead-tin eutectic) are always spherical or near-spherical. We never saw evidence of liquation of lead or its appearance in interdendritic spaces, nor did we ever see structures that would indicate working or heat-treating of the bronze.

The metal itself exhibits the typical structure of a high-tin bronze with an α and $(\alpha + \delta)$ eutectoid phase as well as a fair number of inclusions. As evident in Figure 3, the large inclusions tend to segregate towards the center of the mirror, while the small ones (some of them sulfides) are evenly distributed throughout the matrix.

Our microscopic examination showed that

FIG. 4.—Mirror #4; detail of a crack normal to the surface; ×64, bright field, unetched.

there are three significant regions within the black mirrors—all clearly evident in cross section (fig. 5). The very top surface is a non-metallic layer that appears white or light green in bright-field reflected polarized light. This very thin surface layer merges smoothly and without discontinuity or interface into a band of a modified alloy. In this "altered zone", the α-phase of the original bronze is replaced by a consituent of a different chemical composition, while retaining the original morphology and the original space. It is replacement by volume rather than stoichiometrically. This three-layered structure has been seen by both authors on many samples of dark, shiny objects, both weapons and mirrors.[16]

As the distance from the surface increases, the altered zone gradually turns into the basic alloy. Under higher magnification the *gradual* nature of the transition from the altered zone to the basic alloy is strikingly evident.

The area shown in Figure 5 is located on the back of mirror #4. Effects of "contouring" are usually more pronounced on the decorated back than on the face. The way in which the altered zone follows the contours of the surface layer is quite characteristic and can be seen on many cross sections.

Etching experiments. After the three characteristic regions within the mirror were defined, various etchants were used to study the details of their structures. Ammonium peroxide, potassium dichromate, dilute ferric chloride and Villela's etch were employed. When, later in the study, sulfur prints were used to study the distribution of sulfur compounds within the bronze, the preparation of the sulfur prints produced an additional etching process as shown in Figure 6.[17]

In all cases the etchants were applied to a freshly polished surface of mirror #4, the largest sample at our disposal. None attacked the outermost, non-metallic layer in any discernible way. The effect of the etchants on the altered zone and the basic alloy can be summarized as follows.

Ammonium peroxide revealed the structure of the basic alloy and brought out the particles in the bronze, but it gave only a slight brownish tint to the altered zone.

Potassium dichromate attacked the bronze but only tarnished the altered zone. This led eventually to a noticeable difference in height, with the altered zone and the inclusions in the bronze standing up above the alloy surface.

Ferric chloride diminished the contrast between the alloy and the altered layer; the gradual transition between the two became even more gradual. Parts of the altered layer that were close to the external mirror surface appeared slate grey.

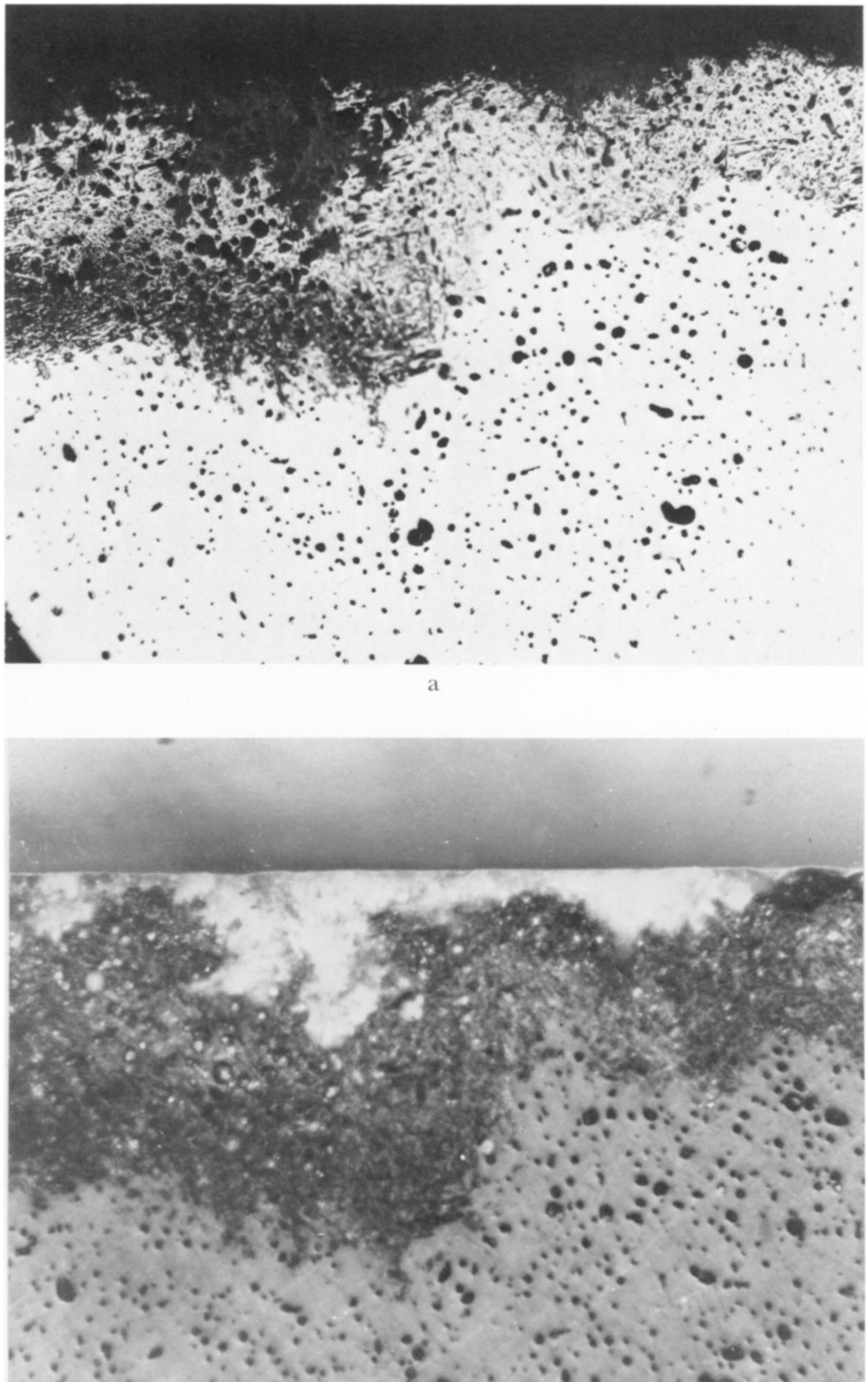
Villela's etch served mainly to bring out inclusions in the matrix and revealed the details of their structure. It did not selectively attack the altered layer.

Electron microprobe studies. A Norelco AMR/3 Electron Microprobe was used to relate chemical composition to the microstructural features.[18] It was operated at 30–40 kV with

[16] W. T. Chase, "What is the Smooth Lustrous Black Surface on Ancient Bronze Mirrors?", *Corrosion and Metal Artifacts—a Dialogue Between Conservators and Archaeologists and Corrosion Scientists*, NBS Special Publication 479, ed. Brown, Burnett, Chase, Goodway, Kruger, Pourbaix, (U.S. Dept. of Commerce, Washington, D.C. 1977); Structured Discussion Question 1, Figures Q-1-6 to Q-1-10, pp. 195–196.

[17] George L. Kehl, *Principles of Metallographic Laboratory Practice*, (McGraw-Hill, New York, 1949).

[18] LaVerne S. Birks, *Electron Probe Microanalysis*, (Vol. 17 of the Chemical Analysis Series, Wiley-Interscience, New York, 1971).



a

b

FIG. 5.—*a*. Mirror #4, detail of the surface, showing, from the top: the glassy layer, the altered zone, and the body metal; ×187, bright field, unetched. *b*. Same as in *a*., in reflected polarized light.

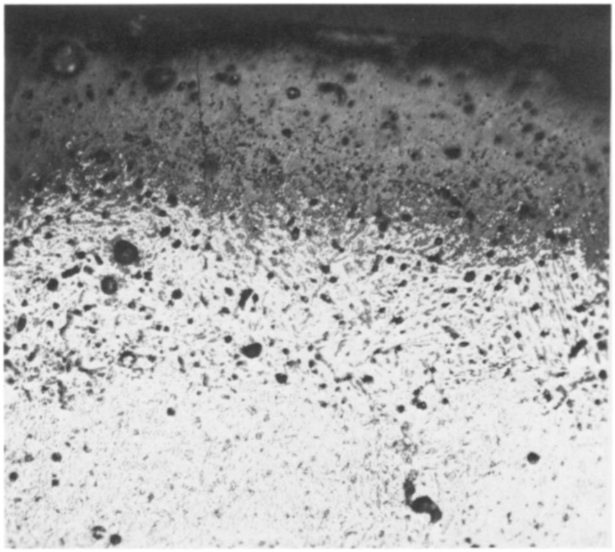


FIG. 6.—Mirror #1, detail showing the surface (glassy) layer and the altered zone; ×258, bright field, etched for sulfur print.

approximately 5.5 mA beam current. The electron beam could be focussed to ca. 3 μm diameter, but because of the coarseness of the structure, a 10 μm beam was usually employed. Sample surface observations were made at magnifications up to ×60 in polarized light. The 6° take-off angle of the instrument imposed fairly stringent requirements as to surface flatness; detection sensitivity of the flow-proportional counter and resolution of two bent-crystal spectrometers were excellent.

Elemental beam scans for Cu, Sn, and Fe on mirror fragment #4 are shown in Figure 7. The beam path was approximately normal to the surface and the sample was driven at a rate of 125 μm/min from one side of the mirror cross section to the other.

These traces illustrate the most distinctive characteristic of the black mirrors: the

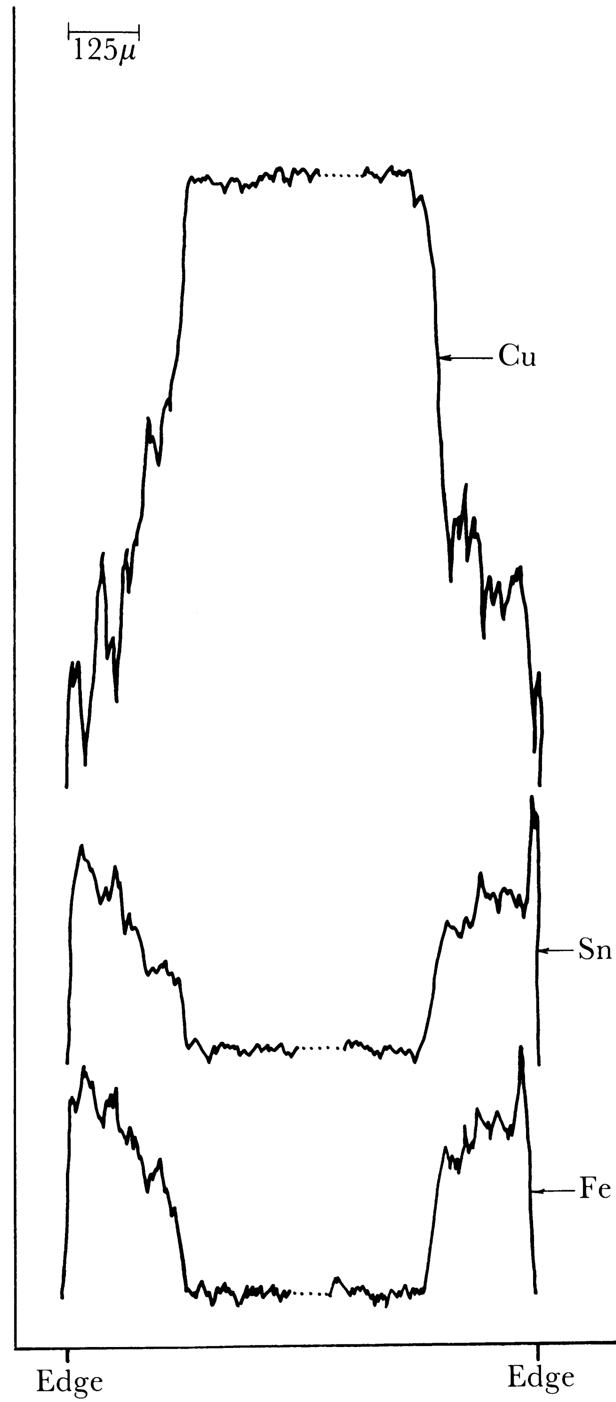


FIG. 7.—Composite of electron microprobe traces showing the composition of copper, tin and iron against a distance across a section of mirror #4. The heights of the traces are proportional to the CuKα_1, SnLα_1, and FeKα_1 intensities. The altered zone and glassy surface are seen to have more tin and iron and less copper than the body metal.

surface region—comprising both the non-metallic layer and the "altered zone"—is of a chemical composition distinctly different from that of the bulk metal. The thickness of this region can vary (thickness range approximately 200–500 μm), but the compositional pattern is always the same: copper, which comprises 70–75% of the bulk alloy, decreases to around 40% in the surface region. Tin, on the other hand, increases from about 25% in the bulk to about 40% on the surface. One finds substantial amounts of iron as well as silicon in the surface region. Iron occurs in the bulk alloy only as an impurity at levels of 1% or less, while silicon can hardly be detected at all in the bulk metal at the center of the mirror.

We have scanned ten fragments of different mirrors, each in several places on a cross section, and have consistently found the same or very similar compositional patterns: the appearance of Fe and Si, the decrease in Cu and the increase in Sn in the surface region.

A representative slower scan, recording two elements simultaneously, is reproduced in Figure 8. It shows the high concentration of Si in the very top surface, i.e., the non-metallic layer. In the altered layer the Si content is still high, but it drops to below 0.05% in the alloy proper. The Sn content, on the other hand, is more or less uniformly elevated in the whole surface region. Two experimental details should be noted: first, because of the lower concentrations present, the silicon Kα line is much more highly amplified resulting in larger apparent fluctuations of the recorded intensities. Second, the tin trace is offset the equivalent of 11 μm to the right to avoid overlapping.

The distribution of Fe in the surface region follows quite closely that of Sn. We found clear evidence of Fe in the inside layers of the cracks—such as the one in Figure 4. One of the authors (WTC) has previously published electron microbeam probe pictures of Sn, Fe, and Si concentrations on the cross section of a similar mirror from the Plumer Collection, which confirm the findings above.[19]

Mirror fragments were also placed into the microprobe with the black mirror surface in the plane of the sample, i.e., with the electrons impinging on the black surface. The top surface of the mirror was non-metallic and electrically strongly insulating. The complete lack of surface conductivity was also demonstrated by the fact that beam traces on the surface remained visible for weeks and did not fade. In order to determine the composition of the sample, all samples were subsequently coated with C, Al or Au. The films were thin enough to permit visual observation but adequate to avoid charge build-up.

Because of the references in the literature we carefully searched for mercury and for any organic compounds that could indicate the presence of lacquer. Organic material decomposes under the electron beam; the resulting contamination of the area is easily detected. Nothing of this nature was observed. We also failed to detect mercury in any part of the fragments.

As the experimental evidence accumulated, speculations arose as to the possible role of sulfur in the formation of the black surfaces. Sulfur was indeed present in most samples but after much probe work it became clear that the sulfur was associated with inclusions which were evenly distributed throughout the alloy. The inclusions frequently exhibited

[19] Chase, "What is the Lustrous Black Surface . . ."

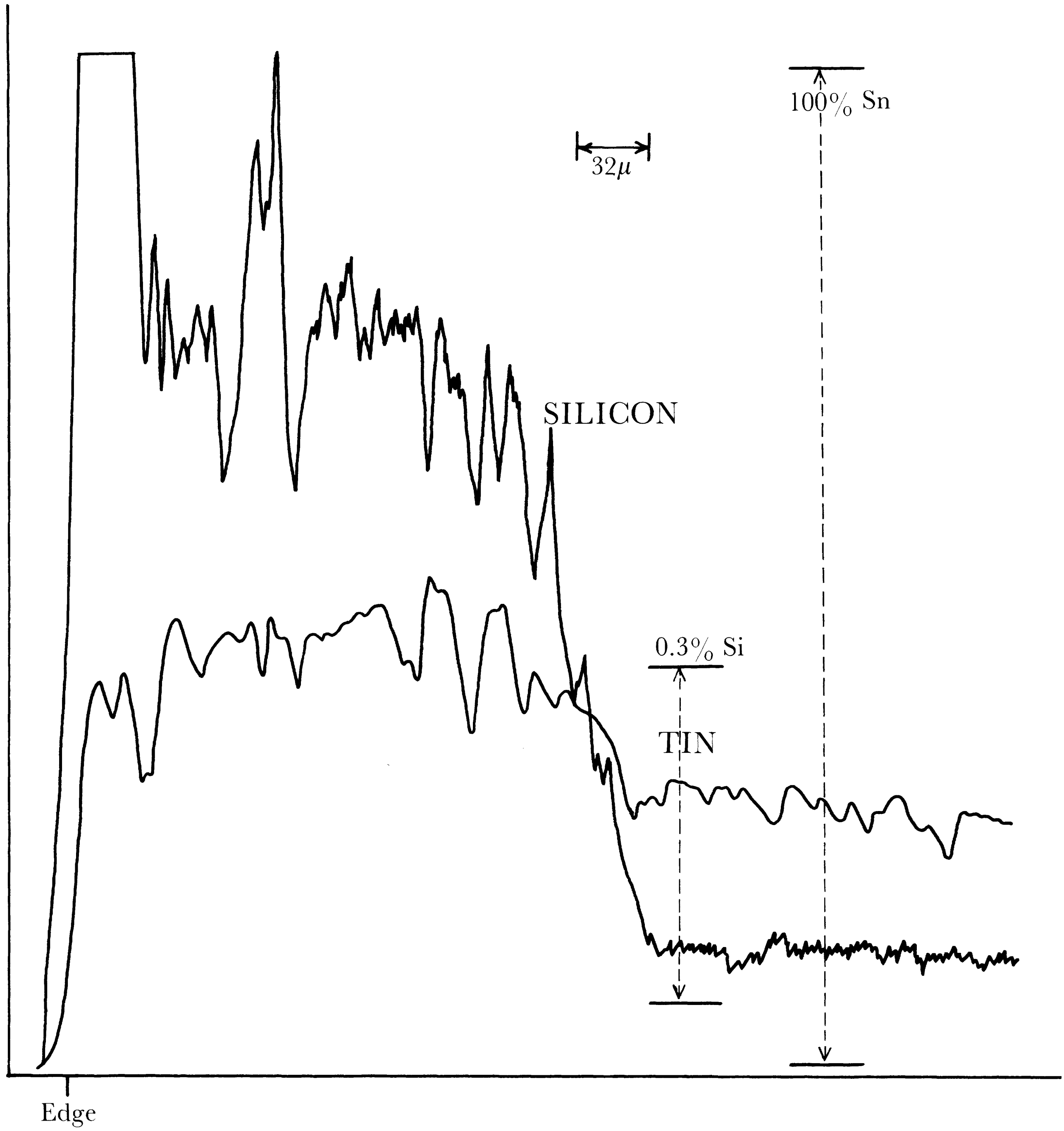


FIG. 8.—Electron microprobe traces showing the SnLα and SiKα intensities across the glassy surface and the altered zone of mirror #4. The glassy surface, ca. 30 μm thick, at left, is enriched in silicon. Silicon is present in the altered zone, and is present only as a trace (ca. 0.03%) in the body metal. The traces were made with two spectrometers simultaneously; the tin trace is slightly displaced to the right to prevent overlapping.

fluorescence under the electron beam. The distribution of sulfur was confirmed by sulfur prints taken on several cross sections.

X-ray fluorescence analysis. All samples at our disposal were analyzed by X-ray fluorescence. Heavier elements were analyzed using a LiF crystal; the lighter elements were detected by a flow counter from the reflection off an ADP or EDDT crystal. A Siemens SRS was in every case operated with an evacuated path. The overall compositional pattern discussed above was confirmed, and impurities such as S, Zn, Co, Mn, Bi, Ag and As were detected (not all impurities in every mirror fragment). It is difficult to utilize this information since we could not assemble the corresponding data for non-black mirrors under the same conditions. Analyses reported in the literature are usually obtained from samples from which "corrosion products" were carefully excluded. This practice, more than anything else, must have prevented Gettens and Collins from detecting iron in the surface layers of the black mirrors.

X-ray diffraction studies. Considerable effort was expended to obtain information about the mirror's surface layer by means of X-ray or electron diffraction. The electron microprobe experiment had shown that the layer is non-conductive; optical microscopy had revealed it to be a white to light green, isotropic, glassy looking substance. Like all others who have studied black mirrors we found it difficult to remove pure fragments of this layer. The intimate interlinking between this region and the altered layer beneath makes it almost impossible to obtain a well-defined sample containing only the non-metallic constituent of the top layer. Even if one were to dissolve the bronze proper using electrolytic or other means, all other inclusions and products of internal corrosion would remain. Therefore, we chose three separate approaches: (1) The plain side of mirror fragment #4 was used directly as a sample in a diffractometer, employing Cr, Cu and Mo radiation. The sample was large enough and flat enough to allow a reasonably accurate recording of the diffraction patterns. (2) A few small surface fragments were dislodged. After slight grinding, they were used as samples in a Debye-Scherrer camera. (3) We also attempted to use the smaller mirror fragment as sample in a Guinier camera.

In the series (1) above, CrKα radiation, being the least penetrating of the X-rays used, gave only faint broad lines around the d-values of 5.16, 3.32, 3.97, 2.60 and 2.50 Å; in addition a few very weak but sharp lines appeared. These lines became stronger as the penetration depth of the radiation was increased by changing to CuKα and MoKα. These lines could be identified as diffraction patterns from the bronze proper. No new lines attributable to the surface layer appeared on the patterns obtained with Mo radiation. The Guinier camera experiments yielded very similar results.

Over the years we analyzed a dozen different powder diffraction samples removed from the top layers of black mirrors. In most of them, we found patterns similar to the one from mirror #1, shown in Table 1: this was a fairly large composite sample of the surface layer containing material from the altered zone as well.

Regarding the identification of these patterns, it is, in general, often difficult to identify certain oxides unambiguously by X-ray diffraction alone. The crystal structure of some metal oxides can be very similar, since the large oxygen atoms mainly determine the packing. Solid solubility of oxides in each other can also be substantial. To

TABLE 1

X-ray Powder Diffraction Pattern Measurements from the Surface Layer of Mirror #1, Compared with Various Oxides.

Black coating #947, 33A #947, 33b		SiO_2 5–0494		SnO_2 21–1250		CuO 5–0661		Cu_2O 5–0667		Fe_2O_3 13–534		Fe_3O_4 19–629	
d(Å)	I/I_1	d(Å)	I/I_1	d(Å)	I/I_1	d(Å)	I/I_1	d(Å)	I/I_1	d(Å)	I/I_1	d(Å)	I/I_1
10.13	1												
8.24	1												
7.17	1												
6.34	1											4.85	8
4.46	2												
4.25	8	4.26	35										
4.03	1												
3.92	1												
3.79	1												
3.67	1									3.66	25		
3.49	1												
3.34	10	3.34	100										
3.19	4												
3.03	4							3.02	9				
												2.97	30
						2.75	12			2.69	100		
				2.64	80	2.53	49						
2.55	1					2.52	100			2.51	50	2.53	100
2.45	5	2.45	12					2.46	100			2.42	8
				2.37	25	2.32	96						
2.28	5	2.28	12	2.31	6	2.31	30			2.28	2		
2.24	2	2.23	6							2.20	30		
2.13	5	2.12	9	2.12	2	1.96	3	2.13	37	2.07	2	2.10	20
1.98	3	1.98	6			1.87	25						
1.82	7	1.81	17							1.84	40		
		1.80	<1			1.78	2						
				1.76	65	1.71	8	1.74	1			1.72	10
1.67	2	1.67	7	1.67	18					1.69	60		
1.66	1	1.65	3							1.63	4		
		1.60	<1	1.59	8	1.58	14			1.60	16	1.62	30
1.54	7	1.54	15										
1.50	1			1.50	14	1.50	20	1.51	27	1.48	35	1.49	40
1.45	2	1.45	3	1.44	18	1.42	12			1.45	35		
		1.41	<1	1.41	16	1.41	15					1.42	2
1.38	6	1.38	7	1.38	19								
1.37	7	1.37	11							1.34	4		
				1.32	8					1.31	20	1.33	4
1.29	3	1.28	3			1.30	7	1.28	17			1.28	10
1.26	4	1.25	4			1.265	6			1.258	8	1.246	4
1.23	2	1.22	2	1.21	12	1.262	7	1.23	4	1.226	2		
1.20	5	1.199	5							1.213	4	1.212	2
1.20	5	1.19	2			1.196	2						
1.18	4	1.183	4	1.18	4					1.189	8		
						1.1697	5						
						1.158	3			1.162	10		
		1.15	2	1.15	8	1.156	4						
										1.141	12	1.122	4
		etc.		etc.		etc.		etc.		etc.		etc.	

Note: Except for the mirror black coating, all data is from the JCPDS Powder Diffraction File; card numbers shown under the compounds.

illustrate the problem, we have included in Table 1 diffraction patterns of some relevant oxides. Difficulties of identification are compounded by the fact that in archaeological samples we cannot expect pure oxides.

It appears, therefore, not possible to deduce from the diffraction data the structure of the mirrors' top surface layer, which may, in fact, be essentially amorphous; we have frequently seen quite narrow and sharp α-SiO_2 lines in diffraction samples of mirror surface fragments—through often weaker than in the example given here. This may indicate local recrystallization in the amorphous layer.

The diffraction data *do* permit us to rule out several previously suggested compositions: the surface layer does not contain tenorite, nor any new Cu-base alloy phase; SnO_2 is virtually ruled out as a surface constituent, and so is Fe_2O_3 or Fe_3O_4.

The evidence clearly indicates that the surface material is a glassy, amorphous silicate containing Sn, Fe, Pb and some Cu. Gettens' refractive index determination ($n = 1.78-1.81$)[20] also suggests the possibility of a heavy-metal glass.[21]

Hardness measurements. Figure 9 shows the results of hardness measurements on the cross section of Fragment #4, given in Vickers diamond pyramid hardness numbers. Because of the coarse and heterogeneous alloy, the actual measurements were carried out on a Tukon hardness tester with a spherical indentor and a load of 100g (this procedure was adapted to minimize the effects of local microstructure variations). The radius of the indentation was converted to VHN by using the formula: $VHN = Cp/r^2$ with the radius of the identations, r, in mm, $p = 100$ g and $C = 5.520$. The area tested was adjacent to the one shown in Figure 5. Though the local hardness shows variations, as indicated in Figure 9, an overall trend is clearly discernible—the very top layer is hardest and the altered layer, though harder than the basic bronze, is not as hard as the outside surface. A second set of measurements on the same sample, but in a different location, yielded an average hardness number of 373 (from four different indentations) for the top layer and average hardness of 353 (five separate indentations) for the altered layers. The hardness data illuminate again the process of a uniform and stable mineralization.

The average hardness derived from the alloy metal shown here (341) agrees in magnitude with the hardness shown for a chill-cast 25% tin bronze (ca. 300 Brinnell hardness).[22]

Density measurements. Early in our study we determined the density of several fragments as part of our overall investigation. Density measurements, which are totally non-destructive, can provide useful diagnostic information. Unusually low densities may indicate mineralization, porosity, or internal corrosion; high densities can point to metallic inclusions, etc. The method described by Caley[23] yielded densities between 8.75 and

[20] Gettens, "Tin-oxide Patina . . .", p. 22.

[21] In interpreting the X-ray diffraction data, one should also consider that compounds from glass devitrification may also be present. For instance, see J. Carbo Nover and J. Williamson, "The Crystallization and Decomposition of $SnO-SiO_2$ Glasses," *Physics and Chemistry of Glasses*, vol. 8, no. 4 (August, 1957), pp. 164–168, where a glass of composition 46% SnO, 53% SiO_2 and $n = 1.652$ is cited as yielding an $SnO-SiO_2$ devitrification product.

[22] D. Hanson and W. T. Pell-Walpole, *Chill-cast Tin Bronzes* (Edward Arnold & Company, London, 1951), p. 243, Figure 151.

[23] Earle R. Caley, *The Analysis of Ancient Metals* (Pergamon Press, New York, 1964), p. 44ff.

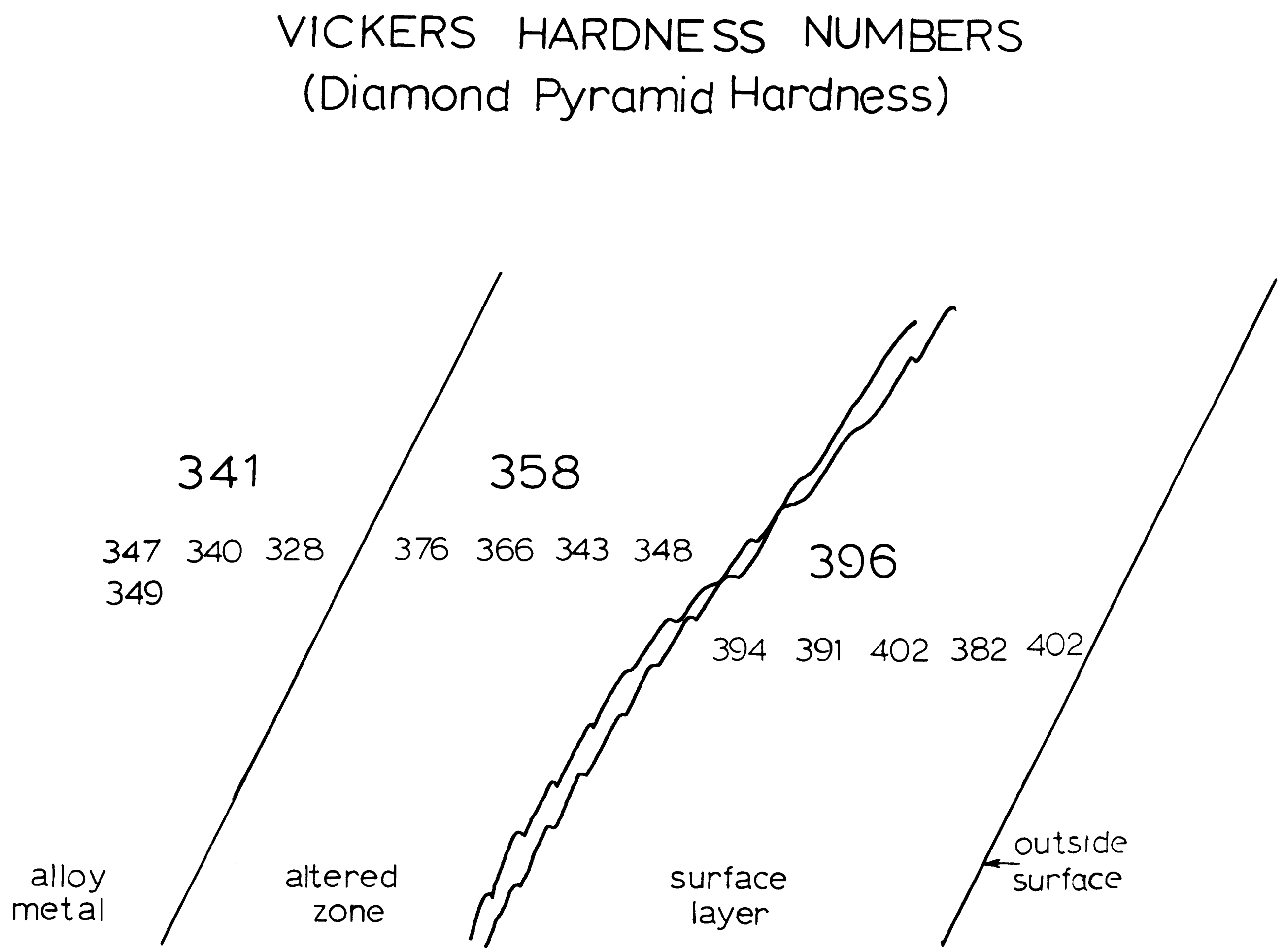


FIG. 9.—Hardness measurements on the surface layers of a cross section of mirror #4.

8.78 kg/m^3. Bronzes of the composition of Chinese mirrors are rarely used in modern times; their extreme hardness and brittleness render them difficult to fabricate by industrial processing techniques. For this reason, it is difficult to find density figures with which to compare the density values from our fragments. A modern SAE 63 bronze (87% Cu—10% Sn—1% Pb—2% Zn) has a density of 8.8 kg/m^3, SAE 64 bronze (80% Cu—10% Sn—10% Pb), a density of 8.95 kg/m^3 [24]. A 25% tin bronze can be seen to have a density of 8.92 kg/m^3 from Hanson and Pell-Walpole's data, which have been redrafted for comparison by Chase and Ziebold[25]. The

[24] American Society for Metals, *Metals Handbook*, vol. 1, 8th Edition (ASM, Metal Park, Ohio, 1961) pp. 1038–1039.

[25] *Chill-cast Tin Bronzes*, p. 253, Figure 167; W. T. Chase and T. O. Ziebold, "Representations of Ancient Chinese Bronze Compositions," Chapter 18, pp. 293–334, in *Archaeological Chemistry* II, ed. Giles Carter (Advances in Chemistry Series no. 171, American Chemical Society, Washington, D.C., 1978).

density range of our fragments is slightly lower than that of the modern bronzes; considering the possible inclusion of oxide and corrosion products in our samples, the data agree quite well.

Summary of the technical evidence. The experimental results from the two cases above are consistent with those from approximately forty other black mirrors examined by the authors, both in Toronto and Washington. About twenty mirrors were examined in detail, and another twenty less thoroughly examined. From all this information, a picture of the "prototypical black mirror" emerges: it is made of a high-tin bronze containing ca. 70% Cu, 25% Sn, and 5% Pb. This alloy is silver-white, melts at around 800°C and is hard and brittle. The prototypical mirror was cast and cooled in a manner no different from other Chinese bronzes: casting sprues, flash, etc. were removed and relief decoration (probably) lightly finished; the remainder of the mirror was given a high polish by the use of abrasives. No working or annealing was performed.

After polishing, the surface of the mirror was in some manner "sealed" and rendered inert to environmental attacks. The "sealing" process gave the mirrors their non-metallic surface, which appears to be an amorphous silicate or mixed oxide containing SiO_2. Below this non-metallic layer, the original bronze structure is significantly altered. The α-phase of an alloy is replaced—isomorphically and by volume—by an iron-containing compound, while the δ-phase remains. Thus, the surface region, both the shiny surface layer and the altered zone beneath, is enriched in tin and depleted of copper. It also contains silicon and iron as major constituents; in the body of the mirror silicon and iron occur only in trace quantities. The surface region is somewhat harder than the mirror itself, and the entire object is very dense and compact throughout. The transitions from the non-metallic layer to the altered zone and from the altered zone to the bronze proper are gradual, with neither interface nor porosity apparent. The non-metallic surface layer is lightly colored and transparent; the black (or brown or green) coloration appears to come from the altered zone seen through the transparent surface.

THE SURFACE LAYER—NATURAL OR ARTIFICIAL?

Approaches to the problem. Was the black surface intentionally produced? To answer this question conclusively, we must examine other dark, shiny bronzes which were (probably) not intentionally patinated. Then we must determine the limits of time and place of the production of the black surface, scan the historical evidence for black mirrors, and compare other metal objects with intentional surface treatments. If the black, shiny surfaces were produced by a craft technique, then this technique would have a beginning and may have a height and a decline; there would be a time before which black mirrors were not produced. We should find a geographical distribution according to production; variations in surface treatment, if intentional, will not be dependent on local environmental (corrosion) conditions. Let us see what evidence there is before attempting to decide if the black of the mirrors is intentional.

Naturally corroded dark, shiny bronzes. Can Chinese bronzes acquire a black surface solely through burial? Dark, shiny surfaces appear on a number of ceremonial vessels in the Freer Gallery.[26] On *p'ou* 13.30, a shiny dark-green tin oxide corrosion product pseudomorphically replaces the metal. The δ-phase can be seen to have corroded first. On *tsun* 25.2, a similar but deeper pseudomorphic replacement has occurred. The tin oxide patina on this *tsun* is very dark olive-green, almost black.

In both cases, corrosion has proceeded with the δ-phase first, leaving islands of uncorroded α-phase. This is the normal order of corrosion for Chinese bronzes. We have no reason to think that these two bronzes were artificially patinated. No glassy layer shows on the surface, and the corrosion product is the usual stained tin oxide.

Turning to excavated material, the *fang yi* inscribed for *Jih Chi*, excavated in 1963 at Fu-feng, Shensi, has a fine shiny black patina spotted with green, matte areas.[27] A bail-handled *yu* dating from the Shang dynasty and excavated at Ninghsiang, Hunan, also has a shiny black patina.[28]

Many more examples of archaeologically excavated bronzes with shiny black or dark green surfaces could be cited. While we have no metallographic sections, as yet, from any of these, it seems likely that the corrosion may be the usual pseudomorphic replacement of the metal with tin oxide, and that the corrosion has probably proceeded with the δ-phase first.

Bronzes with shiny dark surfaces have been recovered from the central loess area of China (Shensi, Shansi and Honan provinces) and from other areas as well, as the *yu* from Hunan, above, demonstrates. It seems likely to us that dark patinas on early bronzes are simply the result of burial. Corrosion on ancient Chinese bronzes usually begins with the loss of the δ-phase; initial removal of the α-phase may well be indicative of intentional patination.

Geographical and chronological limits of black mirrors. While sporadic examples of Shang mirrors had been adduced before,[29] the excavation of the tomb of Fu-hao at Yin-hsü, An-yang, in 1976 proved the existence of Shang bronze mirrors beyond doubt.[30] Four mirrors were found, ranging in size from 12.5 to 7.1 cm in diameter. The front is almost flat, and the simple geometric designs on the back tally with those on other supposedly Shang mirrors. From the photographs in the excavation report, these mirrors do not appear to be black. The context has been dated to the reign of king Wu-ting of Shang by Chinese writers.

[26] Rutherford J. Gettens, *The Freer Chinese Bronzes, Volume II, Technical Studies*, Smithsonian Institution Oriental Studies No. 7, (Freer Gallery of Art, Washington, D. C., 1969), p. 188, Figure 251 and Figure 253.

[27] William Watson, *The Genius of China*, an exhibition of archaeological finds of the People's Republic of China, held at the Royal Academy, London . . . (London, 1973), p. 93 and color plate 93; Anon., *The Chinese Exhibition*, an illustrated handlist of the exhibition of archaeological finds of the People's Republic of China, (National Gallery of Art, Washington, D.C., 1975), color plate 95.

[28] Anon., *New Archaeological Finds in China*, discoveries during the Cultural Revolution (Second edition revised, Peking, 1973), color plate 2.

[29] Doris Dohrenwend, "The Early Chinese Mirror," *Artibus Asiae*, vol. 27, nos. 1 and 2 (1964), pp. 79–98; William Watson, *Ancient Chinese Bronzes* (Faber and Faber, London, 1962), p. 81ff; Sueji Umehara, "Ancient Mirrors of the Yin and Chou Dynasties (Chūgoku in-shu no Kokyō)," *Shirin*, no. 4 (1959), pp. 467–480.

[30] The An-yang Archaeological Team of the Institute of Archaeology, Chinese Academy of Social Science, "Excavation of Tomb no. 5 at Yin-shü in An-yang," *Kaogu Xuebao*, no. 47 (1977, no. 2), pp. 57–98.

The next securely dated group of mirrors comes from the cemetery of the state of Kuo at Shang-ts'un-ling.[31] Kuo was a small state annexed by Chin in 655 B.C.; the cemetery dates from the late Western Chou or early Period of the Spring and Autumn Annals. Two of the mirrors are plain and look like normally corroded bronze (nos. 1650:1.1 and 1650:1.2, diameters 5.9 and 6.4 cm respectively). The third has a design of four roughly drawn animals in relief, and a doubled-ring handle (no. 1612:65, diameter 6.7 cm). As shown in Plate 40 of the excavation report, this mirror looks quite black and shiny. Another object, very probably a mirror, was found in tomb 1052.[32] It shows a back decorated in Western Chou style, which again appears to be black. Two very early swords were also found at Shang-ts'un-ling.[33]

To sum up: while two of the Shang-ts'un-ling mirrors may have the black surface, two probably do not. No analyses or sections have been published from these objects. It is impossible to say whether this black has simply come from burial or is an example of the artificial "mirror black" coating.

In contrast to Western Chou, in Eastern Chou times the number of mirrors vastly increases. Barnard lists 124 mirrors of Warring States date; the total number of mirrors excavated from controlled conditions before 1966 is over a thousand! Barnard also alludes to the need for a re-examination of the chronology of mirrors with reference to the recently excavated material, and he notes the connection of mirrors with the Ch'u state.[34]

While it is true that mirrors are more frequently found in excavations in the Ch'u state areas than elsewhere, the earliest mirrors yet excavated come from Yin-hsü (An-yang) and from Shang-ts'un-ling in the state of Kuo. Dohrenwend, while leaving the question of the Scythian origins of Chinese mirrors open, makes a good case for cross-cultural influence between the northern nomads and the Chinese in determining mirror design,[35] as does Lubo-Lesnichenko.[36] Parallels could be drawn between mirrors

[31] Institute of Archaeology, Academia Sinica, ed., *The Cemetery of the State of Kuo at Shang Ts'un Ling* (Shang Ts'un Ling Kuo-kuo Mu-ti), Archaeological Excavations at the Yellow River Reservoirs Report No. 3, (Academia Sinica, Peking, 1959), p. 77, figures 20 and 21, and plates 23 and 40. Dohrenwend, "The Early Chinese Mirror."

[32] . . . *Shang Ts'un Ling*, Number 1052:56; plate 38, no. 13.

[33] . . . *Shang Ts'un Ling*, p. 84.

[34] "However, a general reappraisal of all investigations will probably be needed before long and it is essential that it should be made with the rapidly growing corpus of properly provenanced finds acting as a means of control. Most of the earliest mirrors reported (Map 10a) come from Late Ch'un-ch'iu sites near Ch'ang-sha, Chiang-ling, and Sung-tzu; there are a number of early Chan-kuo mirrors unearthed in these sites, too, and also in Ch'ang-te. Accordingly, Ch'u would seem to be the area of origin of the mirror. The rapid spread of this new artifact and its general popularity is well evidenced both in the distribution patterns of the chronological maps, and in the rather wide dispersal of site-areas with totals of 15 or more mirrors. Lo-yang has the largest number of mirrors excavated (305); three other site-areas have each reported 100 or more mirrors (3:31, 6:1, and 11:1). [Yu-hsien, Pai-sha-chen, Honan; Kuei-hsien, Yünnan; and Ch'ang-sha, Hunan, respectively.] Altogether somewhat over 1,295 mirrors are entered in the Table of Sites and Remains; the statistics are as follows: six mirrors of Ch'un-ch'iu date have been excavated from three site-areas, 124 of Chan-kuo date from 22 site-areas, and 542 of Eastern Han date from 93 site-areas. Although the average per site-area drops from Western Han to Eastern Han, the marked increase in site-areas with mirrors in the later period is, no doubt, the more significant feature." Noel Barnard and Satō Tamotsu, *Metallurgical Remains of Ancient China* (Nichiosha, Tokyo, 1975), pp. 128–131 and p. 163ff.

[35] "The Early Chinese Mirror," p. 96ff.

[36] E. I. Lubo-Lesnichenko, *Privoznye Zerkala Minusinskoi Koloviny*, Kultura Namodov Vostoka, Mamerialy I Issledovanie, (Akademia Nauk SSR, Glavnaya Redaktsiya Vostochnoi Literatury, Moscow, 1975), pp. 159–165.

and weapons; one especially fine knife of the Scythian type occurs in the Shang tomb of Fu-hao with the early mirrors.[37]

Dohrenwend states that the evolution of Chinese mirrors proceeded through both round and square types made of two plates of metal (so-called "double plate" or "open-work back" types) to the more common solid types which are well-known from the late Chou and Han periods. She places the origin of the double-plate types in Lo-yang or the more northern centers. It is interesting that in this context she mentions the Li-yü style and states that "this might now more accurately be called the Hou-ma style."[38]

Hou-ma is the best-preserved late Chou bronze foundry site which has yet come to light, and the first in which pattern-molds and pattern-stamps have been found. In fact, the production of bronzes and their decor in terms of pattern replication techniques[39] was carried out at Hou-ma in a mature form. Decor in two layers using pattern-stamping is clearly one of the determining factors in the appearance of late Chou Chinese mirrors.

> Once it was discovered that the effect of a superimposed design on a patterned background could be achieved by pressing the rim or the design stamp down harder upon the mold than the pattern stamp, the Huai mirror craft was technically prepared for any design that could be developed upon the former. This stage seems to have been reached with Karlgren's Cl, or in the sixth century B.C.[40]

This is precisely contemporary with the early phases at Hou-ma; a Hou-ma provenance would not be unlikely for the mirrors in Karlgren's A group, especially A2, with a main motif of interlaced dragons surrounded by a border of cowries, nor in the B group, with the sole decoration of monster masks.

None of the mirrors pictured by Dohrenwend in her Group I or II (double-plate mirrors ranging from 7th to 5th century B.C.), nor the mirrors pictured by Karlgren in Groups A and B (his earlier groups) have black patinas. It is only when we get into the slightly later groups whose decoration relates to the style of the Ch'u state that the typical mirror-black surfaces appear. It is interesting that the mirror Dohrenwend reproduces as Plate I, Figure 16 is a late double-plate type, the only double-plate mirror known from Ch'ang-sha, excavated in 1954 from Grave MO11 of the Warring States Period, "Face and decorated back are of different color metal, the former being bluish-black and the latter appearing greyish." This specimen, possibly an import from the north, might conceivably have been the impetus of mirror production in Ch'ang-sha.

Soon after the general introduction of mirrors in the 7th or 6th century B.C., they became a popular item for personal use and, therefore, for tomb burial. Many appear to be black and shiny, judging from the published photographs. One of the authors (WTC) saw some excavated examples in the People's Republic of China on a trip in 1973.

[37] See above; also Max Loehr, *Chinese Bronze Age Weapons*, (University of Michigan: Ann Arbor, 1956).

[38] "The Early Chinese Mirror," p. 85.

[39] Barbara Keyser, "A Technical Study of Two Late Chou Chien," *Bulletin of the American Institute of Conservation*, vol. 13, no. 3 (1975) pp. 50–64, and "Decor Replication in Two Late Chou Bronze *Chien*," elsewhere in this volume.

[40] Doris Dohrenwend, "The Early Chinese Mirror," p. 98; Bernhard Karlgren, "Huai and Han," *Bulletin of the Museum of Far Eastern Antiquities, Stockholm*, no. 13 (1941); *idem*, "Some Pre-Han Mirrors", *Bulletin of the Museum of Far Eastern Antiquities*, no. 35 (1963), pp. 161–169.

A number of mirrors from the Ch'ang-sha excavations were then housed in the Study Museum of the Institute of Archaeology (Chinese Academy of Social Sciences) Peking; they are indeed black and shiny.

Of the mirrors excavated in Hunan, 79% are black; this is a slightly greater proportion than those from Lo-yang (71%) and much greater than those found in Szechuan (39%).[41] It should, however, be pointed out that about 30% of the mirrors counted for Hunan are Chou and Early Han types; only 6% of those for Lo-yang were of this period; more are Han Dynasty mirrors.

Of three mirrors from the Man-ch'eng tombs of Liu Sheng, Prince of Ch'ung-shan, and his wife (Former Han Dynasty), two were shiny and black; one (the smallest of the group) was not.[42] The conditions in the Man-ch'eng tombs were quite dry and favorable for the preservation of metal objects.

As stated above, the entire history of Chinese mirrors deserves another more careful look on the basis of the archaeological evidence, with an eye to intentional surface treatments. While this brief survey can only serve to whet one's appetite for a really definitive study, one can draw some clear inferences concerning the black mirrors.

(1) Both black, shiny mirrors and mirrors without the black surface occur in archaeological excavations of Chou and Han sites in China. Sometimes, in fact, both have been excavated from the same context.

(2) The black surface is seen on many mirrors excavated from the ancient domain of Ch'u. It seems to be more common on pre-Han southern mirrors, and to spread throughout China on Han mirrors. Whether this impression will be confirmed by the archaeological evidence remains to be rigorously tested.

(3) Black mirrors are seen dating from at least as early as the beginning of the Warring States period, and they continue into the Han dynasty.

(4) Mirrors were easily transported over great distances and were much in demand. The mirrors from the Man-ch'eng tombs comprise one type each from Karlgren's categories F, J, and K; F is a category he assigns to the Shou-chou region, while J and K are assigned to the Lo-yang region. All three categories date from the 2nd century B.C.[43] The only unusual features of these mirrors are their size and their northern provenance, 400–500 miles from the putative places of manufacture. A fragment of a typical TLV mirror, apparently with the black surface, was found in Pazyryk (along with Sarmatian silver and unornamented bronze mirrors) some 1650 miles from Lo-yang.[44]

The hypothesis of an intentional surface blackening technique, first widely used in

[41] Hunan Provincial Museum, *Hunan Ch'u-t'u T'ung-ching t'u-lu* (Bronze mirrors excavated from Hunan), (Wen Wu Press, Peking, 1960); count 119 (79%) black, shiny, 32 (21%) not; Lo-yang Shih wen-wu-kuan-li; wei-yuan-hui, *Lo-yang ch'u-t'u ku-ching* (Wen Wu Press: Peking, 1959), count 74 (71%) black, shiny, 30 (29%) not; Szechuan Provincial Museum, *Szechwan Sheng ch'u-t'u-tuang-ching* (Wen Wu Press: Peking, 1960), count 29 (39%) black, shiny, 45 (60%) not; see also Karlgren, "Some Pre-Han Mirrors"; Jan Fontein and Tung Wu, *Unearthing China's Past.* (Boston Museum of Fine Arts: Boston, 1973), p. 79 and 80.

[42] Anon., "A Report on the Excavations of the Han Tombs at Man-Ch'eng (*Man Ch'eng Han mu Fa Chüeh Chi Yao*)," *Kaogu*, no. 1 (1972) pp. 8–18; Chase, "What is the Smooth Lustrous Black Surface . . .," p. 185, Figure Q-1-1A and color plate O.

[43] Karlgren, "Huai and Han."

[44] Sergei I. Rudenko, *Frozen Tombs of Siberia: The Pazyryk Burials of Iron Age Horsemen*, translated by M. W. Thompson (University of California Press: Berkeley and Los Angeles, 1970) plate 70.

Ch'u and spreading to all China after the Ch'in unification and the beginning of Han, is not contradicted by the conclusions above. The evidence, especially that of differently colored mirrors in the Man-ch'eng tombs and the black mirror in Pazyryk, where corrosion conditions would have been vastly different than in central or south China, weighs against the black being a natural corrosion product.

THE ORIGINAL COLOR OF THE MIRRORS

Material evidence. To determine the original color of the mirrors, we must bring to bear all the material, literary, and pictorial evidence available. The material evidence is described above. The mirrors (and some of the weapons) are made from a high-tin bronze (ca. 70% Cu, 25% Sn, 5% Pb). This alloy is hard and silvery white when cast and polished. It makes a fine mirror.

The present color as seen on the black mirrors is due to the attenuated reflection of light from a black (non-reflective) or slightly colored layer underneath a glassy surface. The surface is lustrous and transparent or tinted slightly green as seen in section, while the altered zone underneath is black with shiny metallic islands of remnant δ-phase. The very nature of the non-metallic surface layer seems to assure that the basic composition of the altered zone was present when the surface treatment was executed and the surface was "sealed" by applying the glassy surface layer. Warty corrosion, as seen at breaks and pits in the surface layer, lends credence to this statement. The amount of iron in the altered zone also suggests that the layer, when new, contained black or dark iron oxide.

A very interesting piece of evidence arose when we were examining mirrors by radiography for a projected catalogue on Chinese mirrors in the Freer Gallery of Art. The backs of at least three mirrors (F.G.A. nos. 09.275, 16.244, and 11.104) were seen to be black in some areas and silvery in others; these areas are related to the design. In Figure 10 we reproduce one of these mirrors (*a*) in normal light and (*b*) in diffuse reflected light ("tent" lighting). Most of the back of the mirror is black, but the decorative ring in the outer rim, the four bosses and four animals in the middle decor register, the ring around the central quatrefoil and the quatrefoil itself are silver in color. The front of the mirror has apparently been repolished. The selective coloration of the back must be intentional. While mirrors with adventitious black areas, possibly due to corrosion, are also known, it seems certain that the mirror in Figure 10 has been colored to enhance the design.

Subsequent to our discovery of the particolored nature of these mirrors, we noticed a photograph of a mirror from Ch'ang-sha, of the late Chou type, which has a design on the plain concave zone between the raised rim and the decorated back.[45]

The motif of double-pointed lozenges, so well known from early Han textiles, has been applied to the rim of this mirror in black and silver colors; at least, this is what the photograph seems to show. Controlled partial coloring, similar in intent to two-color gold and silver surface treatment, must have been within the technical competence of the Eastern Chou metalworker.

One further note on the material remains seems in order; we know of no reason for a

[45] Hunan Provincial Museum, *Ch'u-t'u T'ung-ching*, . . . no. 25.

a

b

FIG. 10.—Two views of a parti-colored mirror (Freer Gallery of Art 09.275, × .6). *a.* shows the mirror in normal illumination for photography. *b.* shows the mirror in diffuse specular reflected light. The intentional nature of the silvery and black coloration is apparent.

mirror of the standard composition to corrode any differently from a bronze of slightly lower tin content, such as an ancient Chinese vessel. The range of colors and crusty, thick patinas seen on vessels is also seen on the non-black mirrors; when new, these mirrors would have been shiny silvery-white in appearance.

Documentary evidence. While there seem to be no literary sources giving information on the colors of weapons of the late Chou and Han periods, there are literary sources referring to mirrors. Many inscriptions occur on mirrors themselves; these often state that the mirror is bright (*ming*) or bright and shining (*ch'ing-ming*).[46]

In ancient literature, mirrors are often mentioned. Shen Pu-hai, the legalist philosopher of the fourth century B.C., is quoted as saying, "if a mirror has a flawless surface, then without any action, the beautiful and the ugly are revealed in it of themselves." In resembling a mirror, the mind was *ming* (brightly intelligent), or, presumably, *ch'ing ming* (totally clear and brightly intelligent).[47] In a poem by Hsü Kan (171–218 A.D.), the mirror occurs: "Since you went away/my shining mirror darkens with neglect"[48] or "Since you went away/my bright mirror lies dim, untended."[49]

Although the majority of literary sources talk of mirrors that are bright and shiny, some mention black mirrors. T'ang Shen-wei, a pharmaceutical naturalist writing in 1080 A.D., said that silver blackened by exposure to sulfur vapors for several days was used to make "dew-mirrors" for collecting dew at night.[50] The legendary personification of the sun is said to be looking for a bride, "black and shiny like a mirror."[51] It seems logical that black mirrors are mentioned in connection with the moon and night here.

One illustration of early mirrors may have some bearing on the question. It occurs in Ku K'ai-chih's painting, "Admonitions of the Imperial Instructress," in scene 6 shown in Figure 11.[52] On the left a lady, whose hair is being plaited by a servant girl, observes the process in a mirror. The mirror has a tasseled cord and is supported on a stand. It is, perhaps, a foot in diameter. The back, which we see in the painting, is dark or black and is plain with one relief line for decoration.

On the right, another lady adjusts her hair while looking in a mirror. We see her from the back. Her left hand holds the mirror, which shows a clear reflection of her face and upraised right hand. In painting this scene, the artist simply drew a thin black line to delineate the edge of the mirror and drew the face and hand of the lady within it. The painting communicates the bright, shiny,

[46] W. Perceval Yetts, *The George Eumorfopoulos Collection Catalogue*, vol. 2, bronzes, bells, drums. mirrors, etc. (Ernest Benn, London, 1930) p. 30ff and p. 52; Watson, *Ancient Chinese Bronzes*, p. 96.

[47] Thomas A. Metzger, "Ultimate Wisdom, or Applied Psychology? A Review of Creel's Shen-Pu-hai," *Early China*, 2 (Fall 1976), pp. 20–21.

[48] Translated in Burton Watson, *Chinese Lyricism*, (Columbia University Press, New York, 1971) p. 45.

[49] Translated by Ronald C. Miao, in *Sunflower Splendor*, editors Wu-chi Liu and Irving Yuching Lo (Anchor Press, New York, 1975) p. 40.

[50] Joseph Needham, *Science and Civilization in China*, volume 5, part 3 (University Press: Cambridge, 1976), p. 31, Note a.

[51] Catherine Hoppe, "Deux miroirs d'epoque T'ang," *Cahiers de Mariemont*, no. 5 and 6 (1974–1975), pp. 21–30; Marcel Granet, *Dancses et légendes de la Chine ancienne*, (Librairie Félix Alcan, Paris, 1926). vol. 1, p. 507ff.

[52] The painting is now in the British Museum, London; see Osvald Sirén, *Chinese Painting*, (Lund Humphries, London, 1956) vol. 3, plate 13.

FIG. 11.—A detail of Ku Kai-chih's painting, "The Admonitions of the Imperial Instructress," showing two ladies at their mirrors (after Sirén); the original is in the British Museum.

clear reflection as we see it in polished speculum bronze, without any coloration at all.

Possible uses of black mirrors. Let us sum up the available evidence. Not all ancient Chinese mirrors have the mirror black surface. Mirrors with two-colored surfaces can be found. Mirrors with shiny white surfaces which have corroded can also be found; a shiny white mirror is represented in the Ku K'ai-chih painting.

What possible reasons would there be for mirrors to be black? As far as we can tell, mirrors were used in ancient China (late Chou and Han times) for the following purposes:

(1) Cosmetic uses—examining one's own reflection
(2) Collection of dew from the moon at night[53]

[53] Joseph Needham, *Science and Civilization* . . . vol. 4, part 1 (Section 26), p. 87ff.

(3) Burial with the dead[54]
(4) Burning glasses[55]
(5) Optical experiments
(6) Magical purposes[56]

For cosmetic purposes, some mirrors were shiny and bright (not black) as we see from the Ku K'ai-chih painting and the quote from Hsü Kan's poem. Of course, the back could be black, but the face had to be shiny and reflective. Hsü Kan's poem also shows conclusively that some mirrors corroded in a relatively short time (months to years). These must not have had the corrosion-resistant black surface. The corrosion (and polishing) of cosmetic mirrors was, in fact, familiar enough that Hsü Kan could use it as a poetic metaphor.

Dew-collecting mirrors (or at least some of them) were black. While it is not clear when mirrors began to be interred with the dead as a symbol of light, the later uses, as de Groot outlines them, imply the use of bright mirrors.

Magical purposes do not, it seems to us, imply either black or silvery mirrors. It is not clear whether the surface-blackening and coating would disturb the light reflecting and focussing property of one of the so-called "magic" mirrors or not; our guess is that it would not.[57] Other magical powers are ascribed to mirrors by de Groot,[58] and it is unclear whether these uses would require light or dark mirrors.

It seems that, on the basis of the material evidence, the evidence from literary sources, and the pictorial evidence, mirrors must have been produced both in the silver-white color and the black color. The mirror of Figure 10, in fact, shows both colors on the back of one mirror.

PATTERN-ETCHED WEAPONS

Another group of bronzes with intentional surface coloration is formed by the pattern-etched weapons. We use the term "pattern-etched" to denote various sorts of surface treatment; some weapons have an all-over coloration, some are partly colored; some have patterns on the blade. Since there seems to be a connection with etching processes, we have decided to use the term "pattern-etched" to apply to the entire class. Watson[59] uses the term "variegated" to apply to these weapons, and says (referring to the Late Chou period):

> To the same enterprising time belong weapons—swords, *ko* and spearheads—decorated with mottling and figures such as the stars on the spearhead of Color Plate C. It is not known how the pattern was produced on the metal surface. Possibly the marks have been accentuated in the patina acquired by the bronze during burial. This *tour de force* of metalcraft may have been an achievement of the Ch'u foundries, for a large number of weapons decorated in this

[54] J. J. M. DeGroot, *The Religious System of China* (E. J. Brill: Leyden, 1897) Vol. 2, p. 398; Vol. 1, pp. 45 and 93; Friedrich Hirth, *Chinese Metallic Mirrors, with Notes on Some Ancient Specimens in the Museé Guimet, Paris*, reprinted from the Boas Anniversary Volume, pp. 308–256 (G. E. Sechert and Company, New York, 1907).

[55] Joseph Needham, *Science and Civilization . . .*, Vol. 4, part 1 (Section 26), p. 90ff.

[56] De Groot, *The Religious System of China*, Vol. 5, pp. 1000–1005; also Needham, *loc. cit.*

[57] On "magic" mirrors, see Needham, *Science and Civilization* . . . Vol. 4, part 1 (Section 26), p. 90ff.

[58] De Groot, *The Religious System of China*, p. 1000.

[59] William Watson, *Ancient Chinese Bronzes* (Faber and Faber, London 1962), p. 66 and color plate C.

manner were recently excavated near Ch'ang-sha in Hunan.

While we have done much less work on pattern-etched weapons than on mirrors, it is worthwhile to compare the two for the light the comparison may throw on intentional surface patination. Some of the weapons are quite plain but, when made, were apparently finished in two different colors. The blade could be black and the handle green or the blade green and the handle black.[60]

While the patina may have changed in burial subsequent to use, the fact is that the two parts now have a different patina; this difference in patina is not related to changes in the metal composition nor anything else we can imagine with the exception of intentional surface treatment of part of the sword.

In Ch'ang-sha, swords of the above type have also been excavated, as have swords with a different-colored stripe running down the median ridge, *ko* with spots on the surface, *ko* with irregular curved patterns ("worm-tracks") on the surface, swords with lozenge-shaped surface decoration, etc.[61]

TECHNICAL STUDIES IN CHINA

The Ch'ang-sha excavation report also contains an analytical table of bronzes.[62] Two swords are listed as having 78% copper, 14% tin, and 1.5% lead, and 72% copper, 14% tin and 10% lead, respectively. A two-color striped sword was analyzed; the edge contained 74% copper, 18% tin and 1% lead, the inside ridge contained 78% copper, 10% tin and 10% lead. (Figures are rounded off from those in the excavation report[63]). A surface-decorated sword from Fu-ling, Szechuan province has also been analyzed. It contained 82% copper, 15% tin, and 1.3% lead.[64]

Another analytical study on weapons was jointly undertaken by the Shanghai Material Analysis Institute and the Technical Laboratory of the Shanghai Museum.[65] The study included three fragments of striped swords, which are of interest in comparison with those from Ch'ang-sha. The fragments showed clear lines of demarcation between the outer (tin-rich) metal forming the cutting edges and the inner (copper-rich) metal forming the spine. The lines run from one blade face to the other, parallel to the plane defined by the two median ridges on the blade faces. Lead in the metal of the spines varies from under 1% to over 10%. Lead is, however, kept low in the exterior cutting edges. The metals of the cutting edge and spine would be different in color, and would probably patinate differently. While we have no analyses of patina on striped swords, some of the high-tin edges appear to have the

[60] For black-bladed swords see the sword in the Hong Kong City Museum and Art Gallery (Reproduced in Chase, "What is the Smooth, Lustrous Black Surface . . ." p. 187 Figure Q-1-2), and sword #1943.52.6 in the Winthrop Collection, Fogg Art Museum, Harvard University; Winthrop Collection Sword Fragment # 1943.52.7 has a fine, thick shiny black patina on the handle and guard.

[61] The Provincial Museum of Hunan, "The Ch'u Tombs of Ch'ang-sha," *Kaogu Xuebao* no. 23 (1959, #1), pp. 41–60 and plate IX, no. 1, 3, 4, etc.

[62] "The Ch'u Tombs of Ch'ang-sha", pp. 59–60.

[63] "The Ch'u Tombs of Ch'ang-sha", p. 48.

[64] The Szechwan Provincial Museum and the Chungking Museum (and Fu-ling Museum), "Excavation of the Warring States Open Shaft Tombs at Fu-ling, Szechwan Province", *Wen Wu*, no. 5 (1974), pp. 61–84.

[65] The results were seen by WTC on display in the Shanghai Museum in 1973 and subsequently confirmed by private communication (letter from Shanghai Museum, April 10, 1978).

mirror-black patination. These swords show an excellent conscious control of metallurgy and properties of the finished object through composition. By casting a higher-tin outside onto a lower-tin spine,[66] the founder has put the metal with the desired composition and properties in the appropriate place. Knowledge and control of physical properties through composition (and the trade-offs involved) is clearly shown in literary sources from the Eastern Chou period.[67] It is also interesting how these swords presage in bronze the later development of iron swords in Japan, with their hardened cutting edges and toughened spines.

The display cited in footnote 65 also included two pattern-etched weapons, one a spearpoint similar to that in the British Museum,[68] but with a diamond-shaped pattern, and the other a sword with plain hilt and no pommel, also with a diamond-shaped pattern.

> The X-ray analysis shows that the specimen from the surface of the sword contains, in addition to the normal chemical compounds of copper, tin and lead from the bronze, two parts of tin and one part of iron. The result demonstrates that the intaglio design is made of tin and iron. This method started late in the period of the Spring and Autumn Annals.[69]

This result shows the same effect as do our determinations on the mirrors; tin and iron are enriched in the surface layers.

PRESENT INVESTIGATIONS

The Brundage sword. This sword is Brundage Collection Number B60.B758 (fig. 12). One author (WTC) examined it closely at the Asian Art Museum of San Francisco on September 29 and 30, 1971. It is of a type very similar to an uninscribed sword from the excavations at Chiang-ling, shown in the Chinese Archaeological Exhibition which visited the United States.[70] The Brundage sword has a ringed hilt and attached disc pommel. The pommel and about 3 cm of attaching bronze were mortised and set onto a tenon running up from the hilt (this feature recurs on another sword from Chiang-ling).

[66] It is not clear whether the outside or inside of these swords was cast first. The order above assumes casting of the higher-melting metal first. A striped and inlaid sword in the Freer Gallery (No. 29.19) shows radiographically that the inside was cast into the outside edges.

[67] In a book of ca. 240 B.C., the following passage occurs: "A swordsmith said, 'white metal [tin] makes a sword hard, yellow metal [copper] makes it elastic. When yellow and white are mixed together, the sword is both hard and elastic and these are the best ones.' But he argued with him, saying, 'the white is the reason why the sword is not elastic, the yellow is the reason why the sword is not hard. If you mix yellow and white together the sword cannot be both hard and elastic. Besides, if it were soft it would easily bend and if it were hard it would easily break. A sword which easily bends and breaks—how could it be called a sharp one?' Now a sword does not change its nature, yet some may call it good and some bad; that is only a matter of opinion." *Lü Shih Ch'un Ch'iu*, Chapter 150, Volume II, p. 158; Translated in Joseph Needham, *The Development of Iron and Steel Technology in China* (The Newcomen Society, 1964; Cambridge University Press, 1975) p. 1. The famous quote from the *K'ao Kung Ch'i* section of the *Chou Li* also shows knowledge of the properties of different copper-tin alloys; see Chase and Ziebold, "Ternary Representations . . ."

[68] See Watson, *Chinese Bronzes*, color plate C.

[69] Analytical result from exhibition label, translated by Celia Hsu, then Assistant Librarian of the Freer Gallery of Art, 1977; confirmed by private communication (see note 50).

[70] CPAM Hupeh Province, "Excavations at Chiang-ling Hsien, Hupeh", *Wen Wu*, no. 5, (1966), p. 36, Figure 13 and Plate 2: see also Anon., *Historical Relics Unearthed in New China* (Wen Wu Press, Peking 1972, late 69).

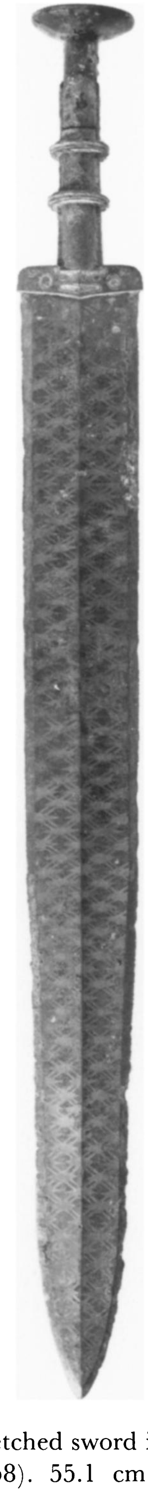


FIG. 12.—Pattern-etched sword in the Brundage Collection (#B60.B758). 55.1 cm long; grey-to-black with green patches and green handle (reproduced by the courtesy of the Asian Art Museum of San Francisco, The Avery Brundage Collection).

FIG. 13.—Detail of the blade of the Brundage sword, showing pattern-etching, possibly employing an etching resist. Ca. × 1.5 (reproduced by the courtesy of the Asian Art Museum of San Francisco, The Avery Brundage Collection).

The blade hilt and guard have corroded normally and now appear green; from the lower corner of the guard (where the surface drops down from the inlaid area of the guard to intersect the bronze blade), the surface is dark grey; this continues down onto the blade. Along the blade the surface is dark grey with occasional green corrosion products, as are the blade edges. The division between the green and grey areas is straight and sharp, and does not coincide with any change in the metal itself.

The design of the pattern is a double-line diaper with diamonds at intersections. The lines of the pattern are beautifully straight and regular (fig. 13); a straightedge can be laid along the lines. The diamonds, however, are not as regular; their edges are ragged where the lines intersect them. In this case, resist etching is a definite possibility. If one takes a fairly hard resist and attempts to scratch this sort of pattern into it (as we have done), the resist tends to break up along the directions of the lines as the diamonds are scratched in. From examination at higher magnifications, it is apparent that the lines and diamonds lie below the background. The pattern is matte black, and much less shiny than the background (fig. 14a). Where the pattern intersects the edge of the sword, small, dark, almost uncorroded areas can be seen (fig. 14b), which suggest that the sharpening of the beveled edges has cut through the structure of the pattern.

The normal cast dendritic structure of a Chinese bronze shows on this sword, and can be clearly seen under even moderate magnification. Dendrites run continuously through both etched and unetched areas, and through the dark spots on the beveled edges. In the pattern-etched areas, however, the α-phase of the dendrites stands above the δ-phase which has been removed (figs. 14c and 14d). This suggests an etch like a strong acid, which would remove the tin-rich δ-phase first.

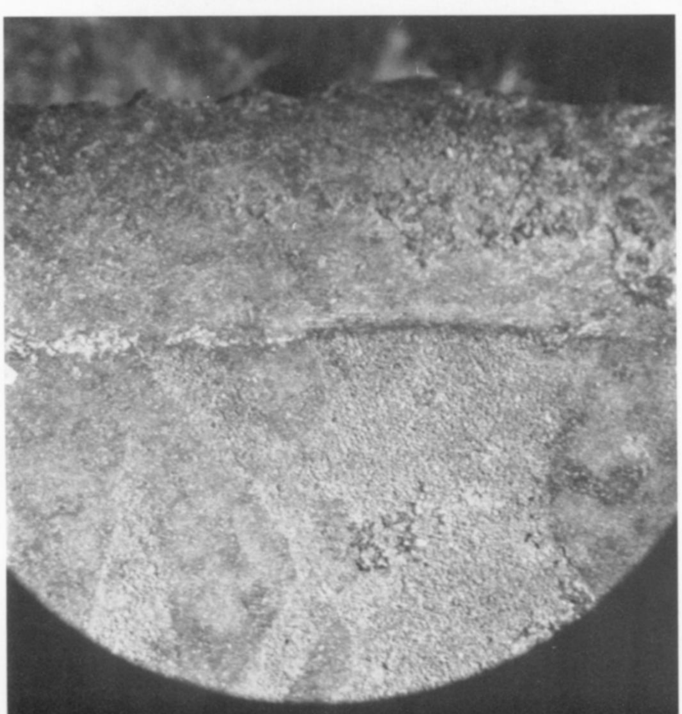
While the above observations of the sword's surface have not been confirmed by sectioning for metallurgical analysis or by replication, they strongly suggest that etching was used to produce the pattern, followed by darkening the surface of the blade.

The Garner spearpoint. The pattern-etched object we have examined most extensively is the Garner spearpoint, Freer Gallery of Art number SC-B-88, (fig. 15). The spearpoint is predominantly green, with a brown pattern of five-pointed stars on the blade. It is 24.4 cm long and 3.7 cm wide and weighs 174.4 grams. A prominent median ridge is present, along with animal masks on the sides of the socket and four double-spiral figures in intaglio on the lower sides of the socket. The beveled edges are free of patterning.

Figure 16 shows a reproduction of an X-radiograph of the spearpoint. The original radiograph was reproduced by contact printing; thus, the light and dark values are reversed. Three major breaks were revealed; the break near the socket has been repaired with lead solder. No repair material was apparent in the upper two breaks, and we found that a wooden reinforcement had been put inside the interior cavity with plaster; neither material shows on the X-radiograph. The pattern-etched design is just visible in the central area; porosity can be seen throughout the blade, and the regular shape of the interior cavity is nicely visible.

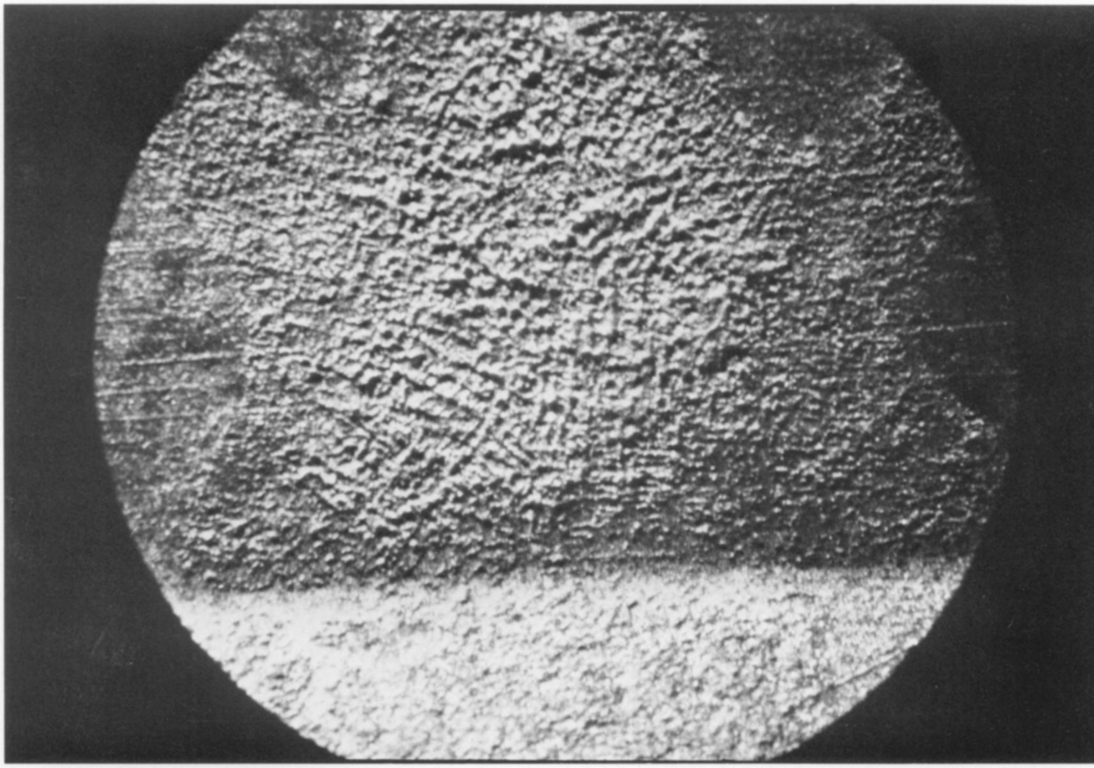
After radiography, the object was disassembled along the old breaks and, after photography of the surface, a section was taken slightly over halfway through the blade.

a



b

FIG. 14*a–d*.—Four magnified details of the Brundage sword *a*. Blade and edge of sword, showing sunken nature of lines, ×6.75. *b*. Edge of sword, showing corrosion-resistant area, ×18. *c*. Edge of sword, showing dendrites in pattern-etched area; the α-phase remains, ×39. *d*. Another area similar to 12*c*, showing the continuity of the dendritic structure from the sharpened area throughout the corrosion-resistant area into the etched area; ×39.



c

d

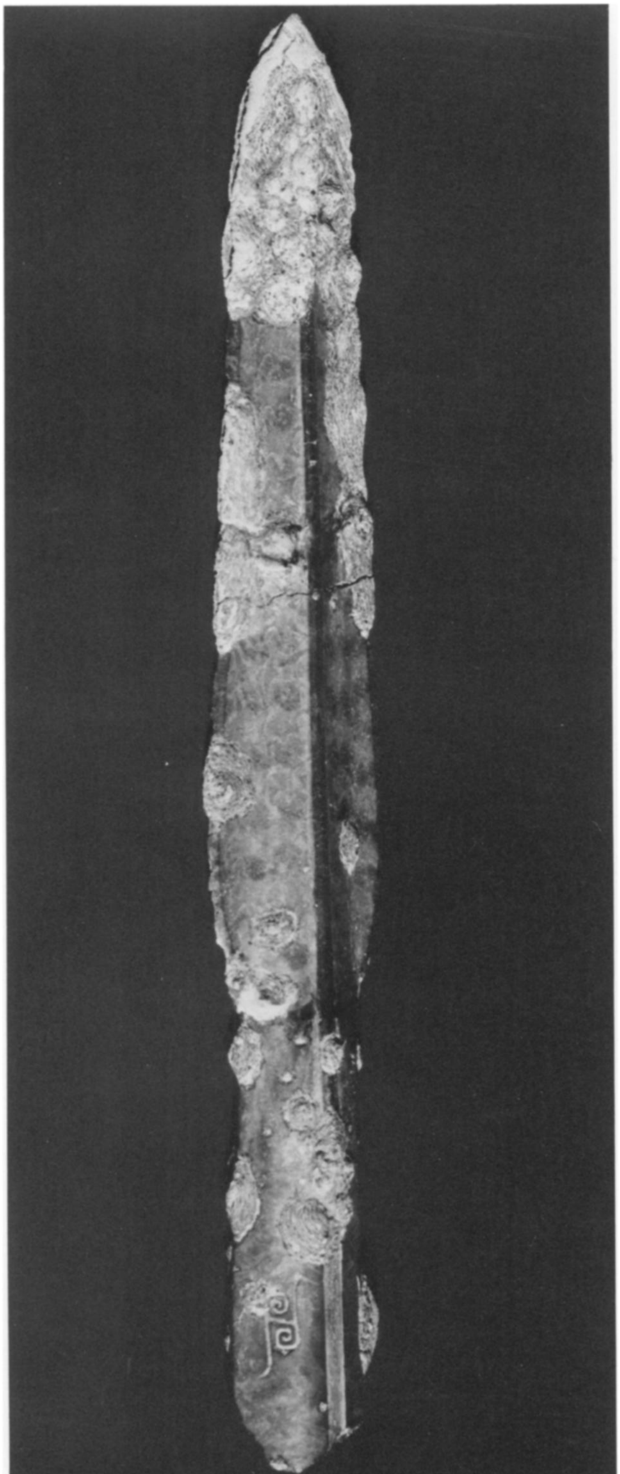


FIG. 15.—The Garner spearpoint (FGA SC-B-88), showing corrosion and surface decoration; slightly reduced.

The upward pointing arrow in Figure 17 shows the area sampled.

A polished metallographic section was made of the sample, and an all-over view is shown in Figure 18, in bright-field, unetched, taken from a photomosaic made at ×20 magnification. The section shows the blade edge on the left and the median ridge at the top. Much cracking and intergranular corrosion can be seen. The most corrosion has occurred at the blade edge. Corrosion can also be seen to be penetrating along cracks in the metal. The dendritic cast structure is clearly revealed by natural corrosion etching.

In a closer view of the sharpened blade edge, Figure 19a, bright field, unetched, we can see that the corrosion along cracks at the blade edge is proceeding with the δ-phase first and the α-phase second, i.e., the tin-rich phase is corroding first, leaving the copper-rich phase in place. Areas of redeposited copper, especially in holes (due to casting porosity or lead removed by corrosion) can also be seen.

When we move to an intact area of the blade, however, we can see that the corrosion or surface treatment on the outer faces of the object has proceeded by the inverse corrosion process. Figure 19b shows an area contiguous to that shown in Figure 19a. The tin-rich δ-phase remains just under the outer (lower) surface.[71] The same corrosion phenomena are seen in the black mirrors.

A polished thin section was then made from the sample shown above, so that the corrosion phases could be studied in transmitted light. A sample from the crack shown in Figure 19b at the lower right shows clearly the difference in the two types of corrosion (fig. 20). Figure 21 shows a similar area at a

[71] Chase, "What is the smooth lustrous surface . . ." Figures Q-1-13 to Q-1-17.

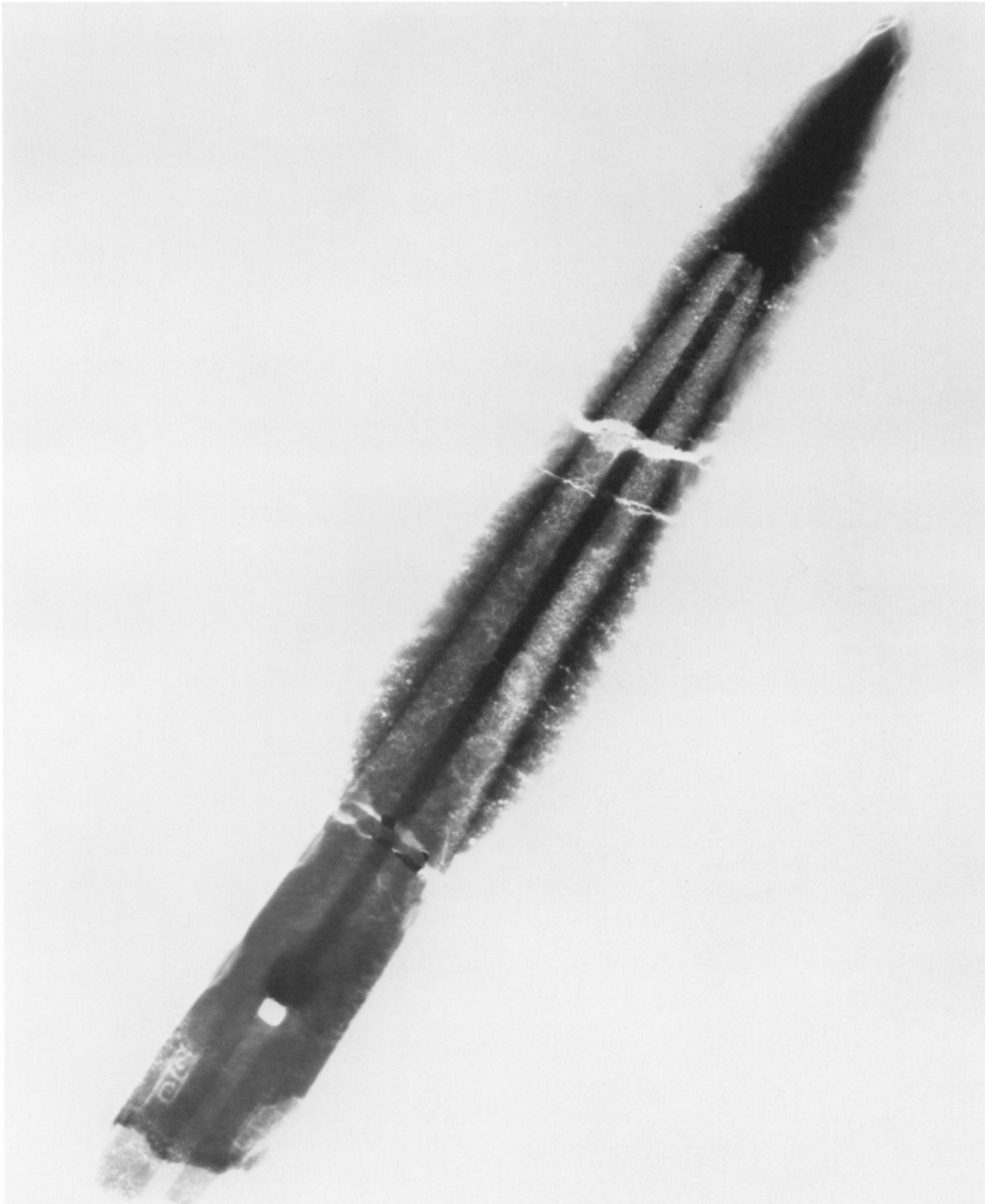


Fig. 16.—Negative reproduction of a radiograph of the Garner spearpoint, showing the interior cavity, breaks and repairs, etc. Radiographic conditions: FGA Radiograph #151, done at Naval Ordnance Laboratory, 8/2/71. 200 kVP (self-rectified unit), 10 mA. Exposure time: 1 minute. Tube—film distance, 6 ft. Type M film, X-omat development. Lead screens used. Actual size.

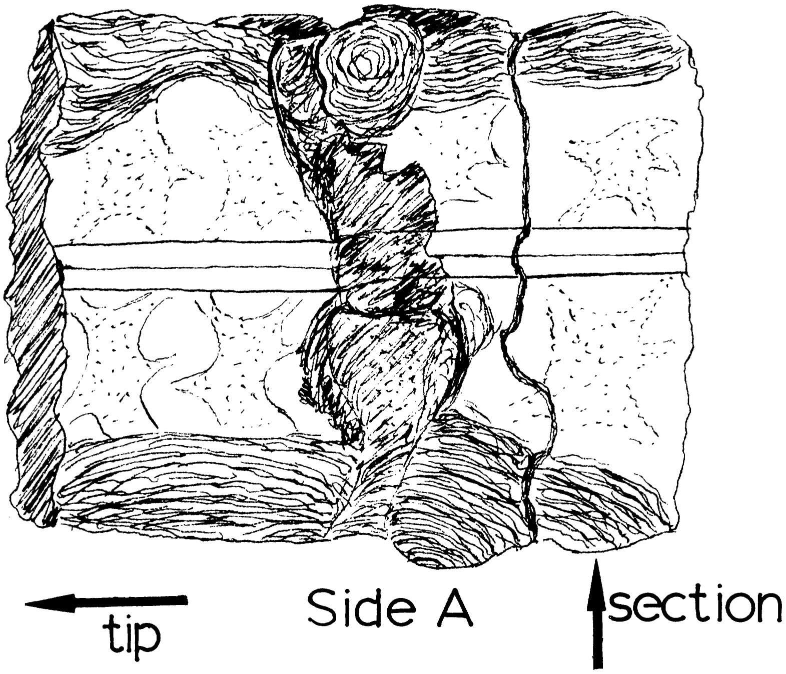


FIG. 17.—Drawing showing area sectioned on Garner spearpoint. The upward-pointing arrow shows area sectioned.

lower magnification, in a combination of bright-field reflected and bright-field transmitted illumination. The clear, greenish surface layer exhibits no birefringence in crossed polars, and appears to be isotropic. The glassy phase seen on the outer surface of this weapon also appears on polished thin sections of mirrors. Underneath the glassy phase, and interpenetrating with it, is the altered zone produced by the α-removal type of corrosion. Areas under the brown five-pointed star design on the surface can be seen in cross section to be more deeply corroded. This is the only visible difference between design and plain areas on the surface; it corresponds to the X-radiographic appearance of the design as barely visible radiotransparent areas on the film. Less metal is present under the design, but the entire weapon has a glassy, isotropic surface.

The thick corrosion crust visible on the surface of the object (fig. 15) tends to bear out the idea of an intentional surface coating applied after etching. The corrosion is warty, as on the mirrors. It occurs in areas where the surface contour turns sharply, as on the spine, or where any surface film would tend to be damaged mechanically, as at the tip and sharp edges of the weapon. These cracks and breaks would allow the corroding medium freer access at these points, and promote corrosion: cold-working, an alternate reason for greater corrosion, is not present (fig. 19a).

In this case, we can accept the idea of a pattern-etching followed by sharpening and then all-over surface treatment applied to the entire outside of the weapon. The interior shaft hole shows no signs of surface treatment.

A spearpoint from the Bishop Collection of the Freer Gallery (X18) was sectioned and examined with the electron microprobe; while the examination of this object is not yet complete, the initial conclusions agree. The black and green shiny surface is depleted in Cu and enriched in Sn, Fe and Si. The pattern-etched weapons, while more varied

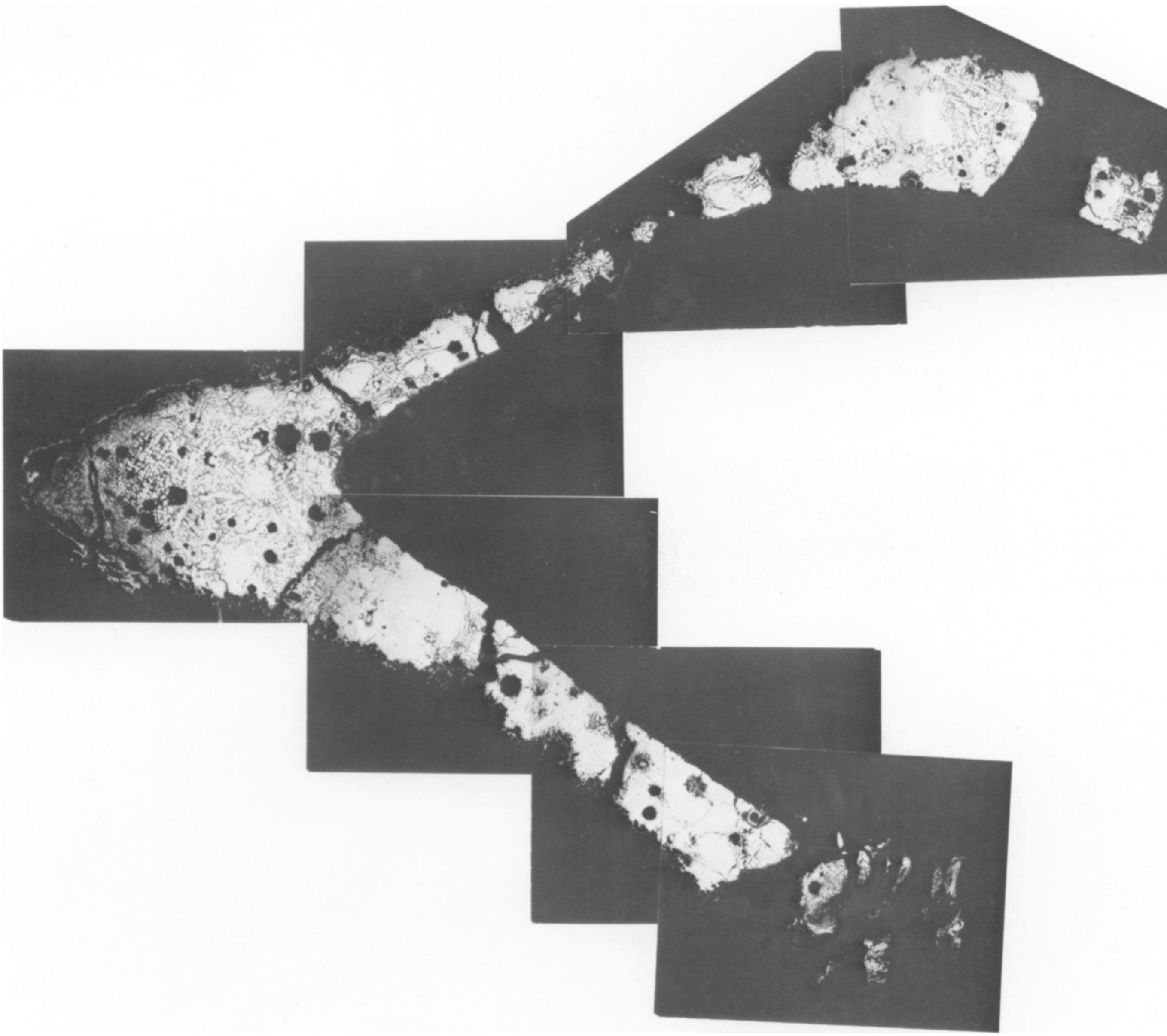
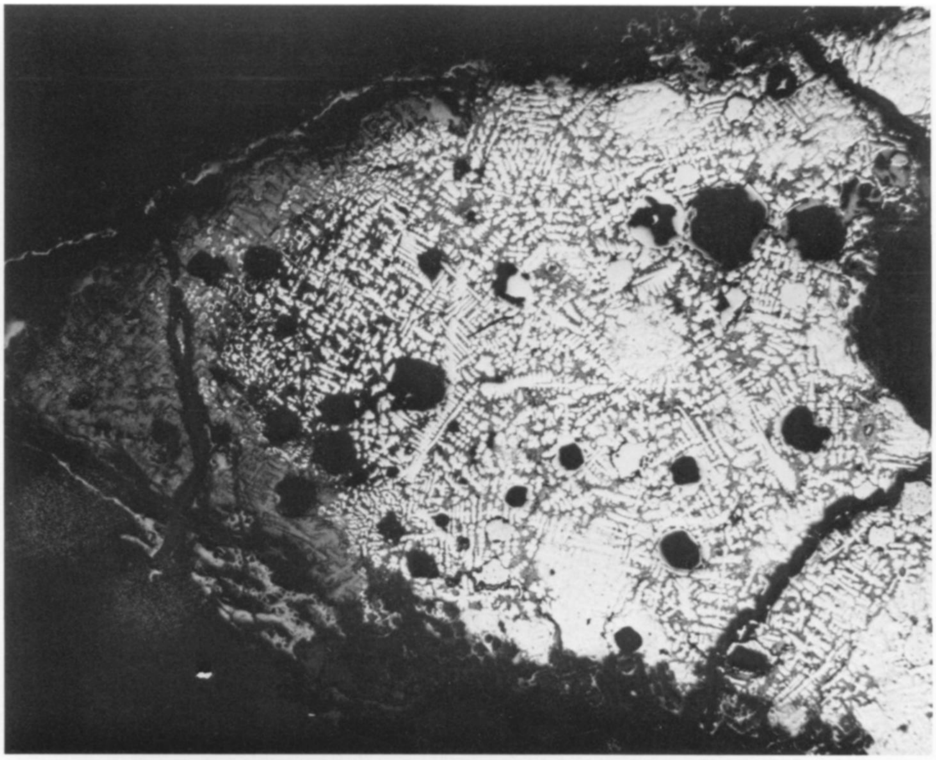


FIG. 18.—Composite metallograph of the Garner spearpoint, ca. ×4, bright field, unetched; the sharpened edge is at left.



a

b

Fig. 19.—Two metallographs of the Garner spearpoint, × 17, bright field, unetched. *a*. Shows the sharpened edge with interior corrosion of the δ-removal type, redeposited copper, cracks, etc. The interior cavity is to the right. *b*. Shows the wall on the blade side of the weapon, the interior cavity is towards the top; note the absence of δ-removal corrosion except at cracks and breaks. The altered surface is towards the bottom of the photograph.

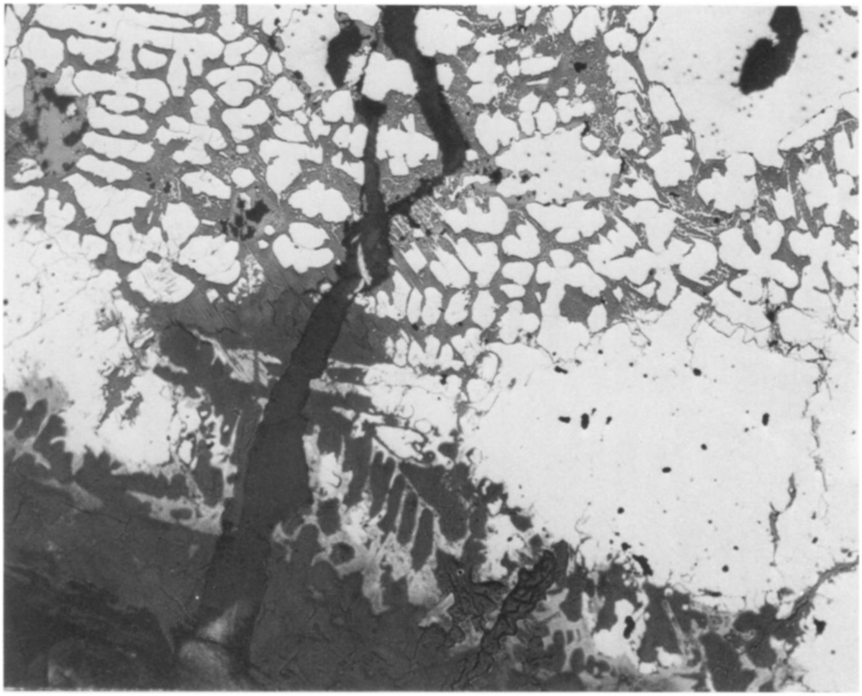


FIG. 20.—A magnified view near the area shown in Figure 19. Note δ-removal corrosion near the crack; the outer surface is shown at the bottom. Remnant δ-phase can be seen under the glassy surface. $\times 100$, bright field, unetched.

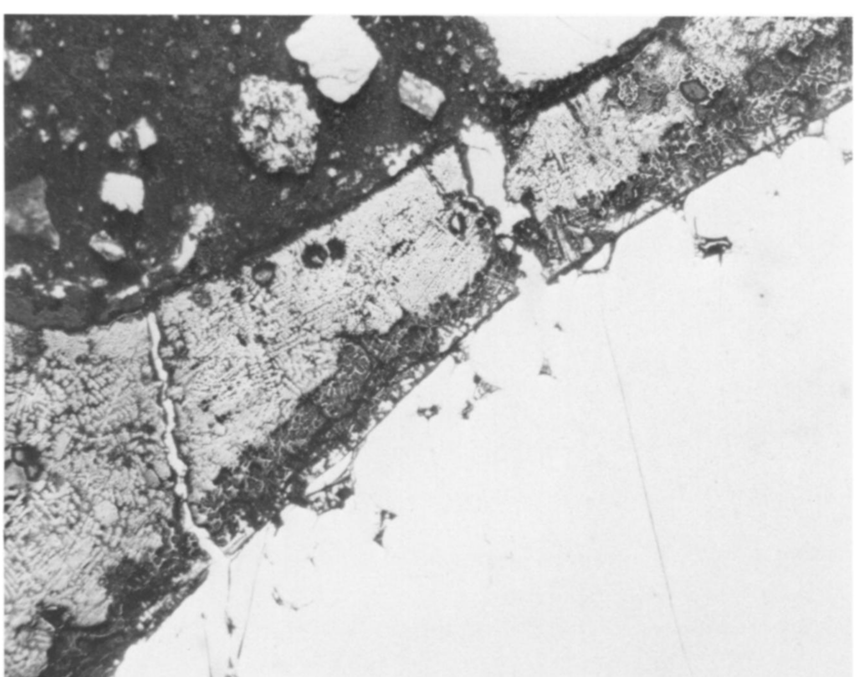


FIG. 21.—A less magnified view in a combination of bright field polarized reflected light and transmitted light ($\times 22$, unetched). The glassy layer can be seen on the lower portions of the specimen.

than the mirrors, certainly point to carefully-controlled surface treatment.

POSSIBLE TECHNIQUES OF SURFACE TREATMENT

THE RANGE OF CHEMICAL SURFACE TREATMENTS

We have shown above that, in the late Chou and Han periods in the Ch'u culture area, mirrors were produced with black surfaces, silvery metallic surfaces, and combinations of these two treatments. Weapons were made with etched decorations, partly metallicized surfaces, and also blackened. From the evidence above, we hypothesize that at least four separate processes of chemical surface treatment were in use:

(1) General surface blackening
(2) Pattern-etching
(3) Spot coloration
(4) Application of a thin, glassy surface layer.

These processes could be applied singly or in combination. Other means of surface coloration were known in ancient China; mirrors occur with gilded, inlaid, and painted surfaces. Indeed, paint resembles the "mirror black patina" in being an applied non-metallic surface. Belt-hooks with gold and silver inlay, gilding in two colors, and stone and glass inlay can be seen in many collections. It is evident that interest in surface coloration and decoration of bronzes was widespread.

This interest in sumptuary encrustation of metals can be clearly seen in objects from the Man-ch'eng tombs.[72] In addition to many gilded and inlaid bronzes, a number of color and surface variations of the bronze metal itself have been found here. Since the tombs were apparently quite dry and well-sealed, and since they were located in a northern area where corrosion is less active than in South China, it seems that the only way to explain the extensive variation in the bronze surfaces lies in the hypothesis of surface treatments of the kinds we suggest.

For example, of three mirrors found at Man-ch'eng, two were shiny black and one a a corroded green. The shiny black ones could have had an application of the surface blackening technique (1) followed by surface glazing (4). The corroded mirror may well have been only silvery when new. The large gold-inlaid *Po-shan-lu* censer has a velvety matte black surface which contrasts with the shiny gold. This could be an example of surface blackening, without the glassy coating. A bronze sword with glassy appearance could show application of the glassy coating on polished metal; some of the other swords have what appear to be glazed edges. We have seen no examples of etched decoration from Man-ch'eng although the manufacture of the dotted *ko* could have involved etching or selective blackening: having no technical evidence to cite, we cannot be sure. A wide variety of very sophisticated metal coloring and finishing processes were employed in these examples of former Han metalwork.

POSSIBLE METHODS USED

While the presence of gilding and inlay is easily recognized after even 2000 years of corrosion, the chemical surface treatments hypothesized above share aspects of natural corrosion processes. The remains of these

[72] See note 42.

treatments are easy to confuse with the results of long-term corrosion; corrosion has also made the task of reconstruction of the intentional processes far more difficult.

All of the chemical processes seem to have been employed for surface decoration after fabrication, or in the last steps of the fabrication process. Mirrors show polishing scratches under the glassy surface layer; the weapons seem to have been etched or surface-decorated, sharpened, and then given their protective surface coat.

The surface blackening and production of the "altered zone" must produce iron enrichment in the altered layer and must remove the copper-rich α-phase, leaving the δ-phase uncorroded. From the penetration of the "altered zone" into surface cracks and from its evenness, it seems that some sort of leaching or cementation process may well have been the technique employed. Since the α-phase at the surface is completely removed, however, and since the metal has not been appreciably heated to an elevated temperature, the process could have taken place in a solution at a relatively low temperature. Ferric chloride (which could be prepared from rust with wine vinegar and salt) will attack the α-phase and turn it brown. Perhaps a prolonged 'etch' would produce the effect of the altered zone.

For etching of the weapons, natural plant acids or an acidic natural salt solution from something like ferrous sulfate may have been employed. Acidic extracts prepared from dried plums were long employed for cleaning ancient bronzes in China.

The spot-coloration techniques appear to be the results of selective tinning; although the experimental evidence for selective tinning is skimpy at the moment, the spots on the Bishop spearpoint look metallic in section; the *ko* from Ch'ang-sha mentioned above have had spots or drops applied; these could have been metallic tin. More proof is necessary on this point.

The production of the glassy surface layer is most difficult to explain. Possible candidates for the "glazing and sealing" process might be a dip in a hot melt of glazing material, rapid heat fusion of a ground frit on the mirror surface, pickling of the surface (producing the "altered zone"), followed by a fusion of the pickled material on the surface (possibly with a flux addition) or a cementation process. Sulfide blackening is ruled out by the appearance of our sulfur prints (above), and by the microprobe analysis. The sulfur distributions in the mirrors occur as sulfide inclusions, remnants from the original ores, and are unrelated to surface treatment. Because of the sharp line of demarcation of the dark material on such weapons as the Brundage sword, and because of the all-over evenness of the coloration, cementation seems the most likely process. Cementation is still being used to produce glassy surfaces on Iranian faience beads.[73] One limit on the glazing and sealing process is that it must have been performed at low temperature; the microstructure of the bronze looks normally solidified, with no evidence of later heat treatment.

None of these processes sounds particularly convincing at the moment; all need to be experimentally studied. We are, inevitably, confused by the effects of time on these objects. Significant alteration takes place during burial as well as in the fabrication process. In fact, we may be defining our

[73] Hans E. Wulff, Hildegard S. Wulff, and Leo Koch, "Egyptian Faience—A Possible Survival in Iran," *Archaeology*, vol. 21, no. 2 (April, 1968), pp. 98–107.

sphere of interest too narrowly. Perhaps we should look more closely at all surface-decoration processes employed in this period (painting, gilding, gilding in two colors, etc.) to see if we can find any clues in information on related crafts.

THE HISTORICAL CONTEXT

While we cannot yet reconstruct, to our satisfaction, the technique involved in chemical surface treatment of bronzes, we can state beyond any reasonable doubt that such intentional surface treatments were practiced in late Chou and Han times. The bronze-maker's art in China undergoes a change from the late Shang and Early Chou. The early emphasis on size, forms which arise naturally from piece-mold casting, and surface decoration which emphasizes the mass and cast shapes of the vessel is replaced by an aesthetic of surface treatment and richness. The number of finishing techniques for metal increases greatly in scope and sophistication.

If we look at other facets of late Chou culture, the same increase in elaboration and sophistication can be seen. Mercury was distilled for the first time.[74] Although the possibility exists that metallic mercury was known earlier in the Near East, its use for fire gilding seems to appear first in China and then to travel through Persia to Egypt and the Roman world.[75] Lost-wax casting seems to begin in China during this period.[76] Glass production starts also.[77] Many of the classic Chinese scientific and alchemical texts date to the Late Chou,[78] as do well-known developments in philosophy, religion, music, war, poetry, representational art, sculpture, and so forth. Probably the most important development was the establishment of the Chinese bureaucratic system of government, which determined the later course of China and her science and technology.[79]

It is difficult to determine the causes of these innovations, or even (at this remove) to say which are causes and which are effects. Since, during the late Chou period, China was broken up into a number of separate kingdoms (the "Warring States"), commerce between them was handled by a rising and upwardly mobile merchant class.[80] Demand from this class influenced the production of sumptuary arts, and must have increased pressure for innovation in metalworking.

Another technical innovation with far-reaching consequences was the development of iron and steel. Iron production begins in China around 600 B.C. and rapidly burgeons into a major industry.[81] The increasing

[74] Joseph Needham, *Science and Civilization in China*, Vol. 5, Part 3, Section 33, p. 4.

[75] P. R. S. Moorey, "Some Ancient Metal Belts: Their Antecedents and Relatives," *Iran*, Vol. 5 (1967), p. 96; P. A. Lins and W. A. Oddy, "The Origins of Mercury Gilding," *Journal of Archaeological Science*, vol. 2 (1975), pp. 365–373.

[76] W. Watson, *The Genius of China*, p. 78.

[77] C. G. Seligman and H. C. Beck, "Far Eastern Glass: Some Western Origins," *Bulletin of the Museum of Far Eastern Antiquities, Stockholm*, no. 10 (1938).

[78] See note 74, above.

[79] Joseph Needham, *Science and Civilization in China*, Vol. 1, p. 94ff and p. 100.

[80] Hsü Cho-yun, *Ancient China in Transition* (Stanford University Press, Stanford, California 1965) p. 127ff.

[81] Needham, *The Development of Iron and Steel Technology in China*, passim; K. S. Chang, *The Archaeology of Ancient China* (Yale: New Haven, 1968), pp. 313–316 and 391; Cheng Te-k'un, *Archaeology in China Vol. 3, Chou China* (W. Heffer & Sons, Cambridge, 1963), pp. 247–249; recent bibliography collected in Li Chung's article elsewhere in this volume.

employment of iron must have changed the role of bronze more to that of a metal primarily for ornamentation and display, and thus must have given impetus to improved methods of surface finishing.[82] The higher temperatures required for casting iron and the waste materials made available by the iron industry may also have contributed to the possibilities for metal treatment.[83] We should not forget, either, that the "altered zone" and surface on the black mirrors is enriched in iron.

The technology of metalworking and metal production (the large-scale manufacture of metal objects and implements) made great strides forward in late Chou times. Metal production is, of course, directly related to ore sources and the metals trade. This may supply us with one reason why the mirrors, with their high-tin alloy, and the high-tin swords, are connected with the State of Ch'u. Many mirrors state, in their inscriptions, that they are made of "metal from Tan-yang."[84] Tan-yang was the first capital of Ch'u, and even in the early first century B.C. was still mentioned as being in the Ch'u region.[85] Modern tin mines are located in South China, in Fukien, Yünnan and Kweichow provinces, with other mines such as the Shui-kou-shan lead and zinc mine located in Hunan, more directly in the Ch'u culture area.[86] In fact, the city of Kuei-hsien, Yünnan, where over 100 mirrors were found, still has an active lead or tin mine.[87] Ch'u was also on the way to the rich tin fields of Malaysia. Tin (as an alloy constituent and as a surface coating) was, probably, more easily available in Ch'u than in the North.

Much more research must be devoted to present and past ore sources in China and their influence on metal production.

The history of Chinese metal technology remains to be written. We are only beginning to gain some insight into the processes and sophistication in use of materials available during the late Chou and Han periods.

The period of the 'hundred schools' of philosophers seems to be the equivalent of the European Renaissance, although the birth here springs, rapid and full-blown, from the Warring States and their background of political turmoil. Experimentation in thought, in the arts, and in technology was widespread. What were the reasons? Was it the free commerce between the various states with their fluid and changing borders? Was it the growing merchant class, socially climbing and interested in the sumptuous arts? Was it the leavening influence of

[82] The transition of bronze weaponry from practical to ornamental use can be seen in the decrease in tensile strength of the alloys used in its manufacture. See Chase and Ziebold, "Ternary Representations . . ."

[83] It is interesting in this connection that a list of materials for making mirrors for presentation to the Great Buddha of Tōdaiji, now preserved as a handscroll in the Shōsōin, mentions the use of the powder given off when iron is forged on an anvil for polishing mirrors. The iron oxide derived from forging, after particle sizes had been controlled by levigation, might not be unlike modern rouge. Masaki Nakano, "Bronze Mirrors of the Nara Period: The Tōdai-ji Chūyō Yōdo Bun'an (Drafts for documents concerning mirrors for the Tōdai-ji Temple) among the archives of the Shōsōin," *Museum* (Tokyo) no. 190 (January, 1967), pp. 2–14, no. 192 (March 1967) pp. 2–13.

[84] A. Bulling, *The Decoration of Mirrors of the Han Period: A Chronology*; Artibus Asiae Supplementum XX (Artibus Asiae, Ascona, Switzerland 1960) p. 46.

[85] Chang, *Archaeology* . . . , p. 395; Burton Watson, *The Grand Historian*, p. 153.

[86] Chiao-min Hsien, *Atlas of China*, ed. Christopher L. Salter (McGraw-Hill: New York 1973), p. 99.

[87] See the quote from Barnard in note 34 above, also.

barbarian and nomadic invasions and customs? Whatever the forces driving late Chou and Han art may have been, the material remains speak to us of lost skills and processes. One can but marvel at the craftsmanship and inventiveness of the ancient Chinese.

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