

laboratory. Here stripping techniques are avoided, mechanical methods being preferred. Deterioration of copper and its alloys can usually be achieved by desiccation (section 3.4.1.1), which should be carried out within forty-eight hours of excavation; but there are notable exceptions (section 5.5.6.1). For long-term stabilization, BTA has been found to be highly effective but even when treated thus, extremely high RH and fluctuating temperatures (especially for enamels) (section 2.4.3), have to be avoided. Bright metal, and objects treated with BTA, should be handled only in gloves.

5.6 Silver and its alloys

5.6.1 Nature of artefacts⁷⁷

Silver (melting point 960.5°C) often contains up to 5 per cent of impurities such as copper, lead, and even iron, but it is also commonly alloyed deliberately, to harden or debase it. Sterling silver is at least 92.5 per cent silver, whilst crude silver may be only 80 per cent pure; very base alloys containing less than 50 per cent silver are termed billon. The distinctive bright white appearance of silver is evident in these alloys, with a tendency to dulling and discoloration with increasing copper content. To make base silver such as billon appear more noble than it is, it is often blanded. Amongst other applied decorative techniques, silver may be gilded or given other yellow surfacings (section 5.1.2.2) and inlaid with black niello (section 5.1.2.5). Glass does not fuse well to silver and so enamelling is rare.

When base silver is worked, the copper content oxidizes, and whilst this is usually removed from the surface by the craftsman, it can remain in the zone just below the surface as 'fire stain'. During its useful life, silverware may develop a much prized dark patina, which can be caused by the uncovering of fire stain as the overlying silver is polished away.

Pure silver can be cold welded but alloys must be soldered with either soft or hard solders (section 5.1.2.1), 'silver solder' being made by alloying silver with copper and sometimes zinc as well. 'Silvering' applied to other metals is usually an alloy of silver with tin (section 5.1.2.2).

5.6.2 Nature of deteriorated material⁷⁸

BLACKENED SURFACE (plate 5.23a). Even in dry air, base silver is tarnished by a layer of copper oxide (section 5.5.2.1), whilst the presence of as little as 2 parts per million of sulphur in the form of hydrogen sulphide or sulphur dioxide, will cause silver itself to blacken by the formation of a protective layer of silver sulphide, argentite (Ag_2S). This sulphide is found on silver from virtually all environments, including the



(a)



(b)



(c)

Plate 5.23. Corroded silver alloys. (a) Silver coin blackened with a protective sulphide tarnish. Fracturing shows the embrittled condition of much ancient silver. (b) Swollen crust of silver chloride on a coin. (c) Right-hand coin shows crust of copper corrosion products on base silver. A similar coin (left-hand) after investigative cleaning

sea. In extreme conditions, the protection afforded by the thin layer of sulphide may fail, and corrosion may continue until all the silver has become silver sulphide.

BLACK/GREY/PINK/LILAC/PURPLE OR BROWN SWOLLEN CRUST (plate 5.23b). Such crusts are composed of a mixture of grey waxy cerargyrite, 'horn silver', silver chloride (AgCl), and brown opaque bromyrite, silver bromide (AgBr), stained to pink hues by cuprite or darkened by silver and copper sulphides. The balance of chloride to bromide is variable, but high-bromide levels would be expected in finds from deposits rich in organic matter. Low corrosion levels lead to the formation of a protective

patina, but higher levels result in a thick, sometimes swollen, crust in which no metal may remain. Marine objects may be covered by such a crust which also includes copper corrosion products, iron oxides, and calcium carbonate. Beneath this may be found either a core of unconverted metal, or else a hollow mould like those found within ferrous concretions (section 5.2.2.3).

GREEN CRUSTS (plate 5.23c). Copper in a base silver alloy corrodes preferentially to the silver, and deposits typical corrosion products both on the surface and between the silver grains (section 5.5.2.1). A base silver alloy on excavation may appear indistinguishable from a copper alloy. In acidic conditions where the copper corrosion products are dissolved away, the remaining silver will probably be blackened.

EMBRITTLED (plate 5.23a). A bright or corroded silver object is often more brittle than would be imagined. There may be more than one cause of this; for example, it may be a result of phase alterations over time or of intergranular corrosion deep within the alloy.

5.6.3 Examination

Where a corrosion crust exists, it may be possible to deduce something about the composition of the original alloy from it (section 5.6.2): thus a thick green crust implies a base silver/copper alloy, whilst a pale, waxy, horn-silver one indicates a purer silver. Details of an original surface may be seen on the outside of a silver chloride crust in a somewhat blurred, swollen state, but in many cases a more accurate representation can be found within the corrosion, much as it can be for copper alloys (section 5.5.2.2).

Silver corrodes intergranularly, with some silver chloride depositing *in situ* and some being extruded; removal of the outside layer of horn silver will reveal an original surface still appearing silver. As corrosion continues, the silver is lost, but the original surface is still maintained by a discontinuity within the corrosion. In a base silver object, whilst the external surface of a copper corrosion crust is uninformative, the original surface may well be perfectly maintained beneath this by the uncorroded silver portion of the alloy; being more noble than the copper, the silver will be cathodically protected (section 5.1.3.2). The analysis of corroded silver alloys is difficult to interpret, for a surface enriched in silver may be a result of several phenomena: for example, corrosion, deliberate blanching, working, and cooling during manufacture, or even silvering a copper alloy. It is possible that this interpretation may be further confused by the redeposition of silver on the surface of a corroding alloy in certain reducing environments.

Radiography will assist in locating engraving, niello, gilding, and the original surface where this is maintained in a corrosion crust by silver.

5.6.4 Cleaning

Once it has been determined that surface blackening is neither a deliberate nor an aesthetically pleasing patina, it should still be removed only when an object is required for display. Not only is it protective, but every time it is removed a new layer forms to be later removed, thereby continually wearing away the metal. When necessary, this removal is often carried out mechanically with extremely fine, soft, abrasive pastes, but excavated artefacts are usually too brittle and cracked to withstand such treatment. For these, chemicals are used, except of course where niello, which is itself silver sulphide, is suspected.

Care is needed in the removal of silver chloride crusts for, as shown in section 5.6.3, the original surface will be maintained, either by weakened silver or by a discontinuity within the horn silver. Cleaning of such material is sometimes done mechanically when, with considerable skill, the outer layer can be picked off the original surface. Alternatively, to avoid scratching any remaining silver, chemicals are used under the microscope; cleaning is halted as soon as the discontinuity or a silver surface appears.

The removal of copper corrosion crusts is carried out chemically since they are much harder than horn silver, and scratching of the underlying metal is difficult to avoid. Moreover, the original surface is likely to be maintained by silver (section 5.6.3) which is not likely to be attacked by the chemicals required to dissolve the copper salts when these reagents are used with discretion.

That silver is a noble metal is useful in cleaning since it remains unaffected by chemicals used, but it is a problem in that dissolved silver (and even copper) is likely to be reduced and plate out as silver (or copper) on the object during cleaning. Thus sequestering agents (section 3.3.2.1), for example thiourea, which remove these metals from solution are used alongside the chemicals used to dissolve the corrosion crusts. Commercial dips containing oxidizing acids are too powerful for archaeological silver and, to break up a crust, organic acids or complexing agents such as ammonium thiosulphate ($(\text{NH}_4)_2\text{S}_2\text{O}_3$), are preferred. Another approach is to reduce overlying silver corrosion crusts to a soft powdery silver, which may then be brushed off to reveal the original surface. This may be done either electrolytically (section 5.1.4.2), or with a chemical reducing agent such as sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) which has been used to treat marine silver in bulk.⁷⁴

5.6.5 Deterioration after excavation

Both horn silver and silver bromide darken on exposure to light; they can change from white to pink, grey, or black within seconds of excavation. In the longer term, excessive UV can superficially reduce horn silver to silver, giving it a metallic sheen. Sulphur is present in the air from industrial pollution, but high localized contamination can arise from rubber, paint, casein glue, wool, cloth finishings, and certain woods. It is not surprising, therefore, that bright silver usually tarnishes, but unless it is heavily alloyed with copper, no other corrosion is likely after excavation. Brittle ancient silver is liable to shatter with poor handling.

5.6.6 Stabilization

5.6.6.1 Passive

To prevent bright cleaned silver from tarnishing, sulphur must be removed from the environment. In the first instance, all materials for display/storage should be tested for sulphur (section 3.4.1.5). Ultimately sulphur can be removed by air-conditioning, but on a less grand scale, hydrogen-sulphide-absorbing materials can be used locally, such as in plugs in vents in showcases or in tissue for wrapping objects. Alternatively, vapour phase inhibitors (section 5.1.5) can be used in sealed cases or boxes.⁸⁰ Close proximity to a source of chloride which will corrode silver must also be avoided. Silver which contains a high proportion of copper can be stabilized by dry storage as in section 5.5.6.1.

5.6.6.2 Active

In the past, in order to debrittle fragile silver, a variety of heat treatments were used, but until further research in this area is published, they should be avoided. Attempts have been made to consolidate objects which have been entirely corroded to horn silver, by reducing them back to silver. This has been done chemically (see note 79) on coins and electrolytically⁸¹ on one famous example at the British Museum, the lyre from Ur, but neither method is as yet routine.

Silver may be treated to retard attack by hydrogen sulphide by the application of a lacquer or a polish which contains an inhibitor (see section 5.1.5 and note 80). Copper in base silver is stabilized by benzotriazole (section 5.5.6.2).

5.6.7 Reshaping

In certain instances deformed silver objects have been reshaped at high temperatures but the technique is limited and cannot be used where

intergranular corrosion has occurred. It is never used until a rigorous metallographic examination has been carried out, both to check for absence of this corrosion and to record the structure which will be lost by this heating.

5.6.8 Summary

Even though silver is a noble metal, when excavated, it can be in a delicate and badly corroded state, worse even than base lead. On site it must be handled with great care and given adequate packing. An original surface may be retained within a corrosion crust, and thus cleaning is carried out only in a laboratory. Since silver is a soft but noble metal, where the metal is to be exposed, chemical cleaning is preferred over mechanical methods. Bright silver is most affected by hydrogen sulphide in the environment and, once blackened, is cleaned only when required for display; it should then be handled only with gloves.

Base silver behaves as a copper alloy, which indeed it is. It is treated in a similar manner to other copper alloys except for cleaning; the original surface of a high-silver/copper alloy is uniquely maintained by noble silver metal. Problems of treatment, interpretation, and analysis of base silver arise as a result of the phenomenon of surface enrichment.

5.7 Gold and its alloys

5.7.1 Nature of artefacts⁸²

Gold in artefacts is seldom pure. One cause of this is impurities from the raw material which, since gold is extremely noble, is in the form of metal, not ore. An important naturally occurring alloy is electrum, or white gold, which has a silver content of more than 20 per cent. This level can be reduced by purification to about 1 per cent, giving a rich red-yellow-coloured metal which is even redder when contaminated with copper. However, gold is usually deliberately alloyed for strength and economy with silver or copper: in this latter case the alloy may be called tumbaga. When gold is mixed with both silver and copper, a pale-yellow base alloy called corinthian bronze⁸³ or green gold may be made. The surface colour of this alloy may be altered by oxidation and/or blanching for decorative effects. Depletion gilding (section 5.1.2.2) of gold alloys in general is common, in order to give the object a rich-yellow pure gold surface. Today the purity of gold is measured in carats, where one carat represents one-twenty-fourth part of the whole.

Gold (melting point 1063°C) is the most malleable of all metals used in antiquity, and without annealing it can be hammered into sheets only 0.2 micrometres thick. It is easily cast and can be joined by cold welding or

gold solder, a binary alloy with 18 per cent copper or a ternary one which, because it contains silver as well, gives a better colour. Alternatively, it may be joined by a technique called colloid hard soldering, whereby the join is made temporarily with a paste consisting of a glue, a copper salt, and water; when set, the joint is heated so that the reduced metallic copper alloys with the gold, forming a bond. Applied gold decoration includes enamelling and niello (section 5.1.2.5-6).

5.7.2 Nature of deteriorated material⁸³⁻⁴

The corrosion of debased gold can be extremely rapid because of the galvanic cells formed with the alloying metals.

BRIGHT GOLD. Gold, being the noblest metal, does not react with any normal environments, and so may be found unchanged on excavation. However, even debased gold, if the quantity of base metal present is slight or if the environment dissolves the corrosion products of the base metal, may be found bright. Where debased gold has been gilded by depletion, considerable corrosion products in the form of black cuprite (Cu_2O) may be formed under the gold surface layer. The metal may well be brittle for the reasons described for embrittled silver (section 5.6.2.5).

SILVER, COPPER, OR IRON CORROSION CRUSTS. Debased gold containing one or more of these metals may become completely obscured by the products of corrosion typical of them.

5.7.3 Examination

By examining corrosion products and metal colours, attempts are made to identify where surface enrichment is present and, if so, whether it has occurred intentionally or not. Likewise, the content of the whole alloy is studied but the simple resort to specific gravity which has been used in many analytical programmes cannot be used on objects with corrosion crusts or casting blow holes. The original surface of objects, although often misleading in colour, will always be represented by the remaining uncorroded gold.

5.7.4 Cleaning

Gold is never cleaned, however gently, without a microscope; the danger of abrasion of a surface-enriched layer or of scratching the soft metal is too great. Care must be taken, then, in the field, to prevent hands rubbing the surface of an object. Even in the laboratory, mechanical cleaning is kept to a minimum, whilst chemicals which remove copper

and/or silver corrosion products must be used judiciously, to prevent leaching of the base metals and dissolution of internal corrosion products.

5.7.5 Deterioration after excavation and stabilization

Gold itself does not deteriorate but alloys will suffer corrosion of the base metal as described in earlier sections of this chapter; they must be stabilized accordingly. Gold can be extremely weak and brittle and must be handled with care.

5.7.6 Reshaping

Like silver, certain gold objects could be reshaped except where there is a fine surface detail or where there is internal corrosion. Again metallographic information will be lost by such treatment.

5.7.7 Summary

Gold should not be polished 'bright' on site; gentle washing alone is permissible. Packaging must ensure abrasion is prevented. Gold alloys encrusted with copper corrosion products also should have no on-site cleaning and are treated as for copper alloys (section 5.5.6).