Chapter 6
Metal Plating, Patination and Corrosion

6.1 Patinas and Corrosion

Surface treatment and patination have been used extensively in ancient and historic metallurgy [68], and practically all metallic substrates are capable of being altered in one way or another. Microstructural studies are often the only way to adequately investigate these surface coatings and patinations. Natural corrosion may, under suitable circumstances, be considered a form of patination, or metals may be deliberately patinated in order to alter surface characteristics. Hughes [26] and Hughes and Rowe [27] make an interesting distinction between four types of surface alteration systems: Firstly, those that rely on a complex metallurgy, but a simple colouring technique in order produce different surface colours. Simple organic coatings are an example used on a wide range of alloys. The second category is the use of a simple metallurgy and complex colouring, the approach taken in the nineteenth century, where fairly standard bronzes or brasses were given a wide variety of colours. Eclecticism, which Hughes [26] says hovers on the edge of kitsch, was used in the late nineteenth century and finally a simple metallurgy and simple colouring such as the oxidized finished on silver and small-scale architectural fittings.

Ancient authors have interesting sides concerning surface appearance, for example, Pliny [44] writes of the artist Aristonidas who sought to capture in a sculpture the madness of Athamas, after he had hurled his son Learchus from a rock: "... he made a blend of copper and iron, in order that the blush of shame should be represented by rust of the iron shining through the brilliant surface of the copper; this statue is still standing at Rhodes" (Natural History 34.40), while Plutarch [45] conducts a philosophical dialogue concerning the attractive blue-green colouration where the bronzes at Delphi possessed a turquoise blue surface patina. For further detailed discussion, see Scott [58]. The deliberate colouration of ancient statues, to make attractive patinated surfaces, has been reviewed by Born [9]. Dark brown or black surfaces were much admired as an alteration to bronze or brass, since additional skill or sophistication was shown by the ability to make golden bronze a dark

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shiny colour and the rarity of it, as in the case of Corinthian bronze, made people carry small statues of it to show off to their friends, as mentioned by Cicero.

Ancient and historic metals may now exist as composite material consisting of metallic remnants and corrosion products. The study of corrosion and patinas is an important part of the description of ancient metals, which has been the subject of numerous papers and books to which the interested reader is referred to here for a great deal of further information which cannot be dealt with in detail in this book, and a basic synopsis is given here (viz. Baas Becking et al. [4]; Berthelot [7]; Bertholon et al. [8]; Born [9]; Brown et al. [12]; Chase [13]; Gettens [20]; Meeks [37]; Scott [58]; Scott and Eggert [67]).

A few general observations will be made here in the context of metallography, but for further reading, see Scott [63–65]. Metallic samples together with their corrosion products must be retained for metallographic examination because they are an important part of the object itself. Corrosion involves the ingress of external environmental factors as well as the outgress of metallic ions to the environment, often resulting in complex layers of corrosion being built up over time, which must be preserved by the metallographer. These diagenetic events are the subject of the works referred to above.

The term patina is generally used for films or crusts of corrosion which are protective, attractive or deliberately produced on the surface of the metal to create a desired finish, colour or texture to the object in question. The production of specific patinas on metallic surfaces has been the subject of many seminal works such as that of Hughes and Rowe [27] to which the interested reader is referred to for more information. A patinated metal may retain the outer morphology of the object in question and may alter the colour to specific requirements, while general corrosion may obliterate or totally obscure the metallic surface.

We can categorize patina and corrosion studies of ancient metals and metallography into several types:

1. The object itself is completely corroded. In such cases a decision has to be made as to whether a sample of the object is worth the effort to mount for examination or not. Some of these totally corroded fragments are interesting or revealing of aspects of fabrication of the original object. They may or may not retain a pseudomorphic morphology of the metallic grains, such as twins, strain lines, nonmetallic inclusions, core material from lost-wax or piece-mould casting, organic material pseudomorphs or traces of organic substances that once touched the object, or which it contained, such as wine or meat. Iron objects may be corroded beyond recognition of the original shape, while gold alloys, silver, copper, lead, bronze and tin are more likely to retain vestiges of the fundamental structural morphology of the artefact. However, corroded cast iron artefacts may still contain components such as ledeburite which are more corrosion resistant and which may be partially preserved as pseudomorphs.
2. The object appears to be visually totally corroded but may have vestigial remnants of original metallic constituents present. These will become evident on polishing and may allow electron microprobe study of the original chemical

composition in cases which outwardly appear hopeless. Pseudomorphs are equally likely as in type I.

3. The object appears to be partially corroded with a possible original surface present. Samples from objects showing this kind of preservation are frequently very informative. Not only is there a substantial amount of remaining metal present, but the interface between metal and corrosion may reveal traces of patination or a distinct junction between corrosion events which have built up over the original surface of the object and corrosion events which have occurred within the metallic matrix itself.
4. The object is visually uncorroded but may be patinated to alter the surface colour or texture. Metallographic examination here may be important, not only for the metallic interior but also for characterization of the patina or coating. Gilding, tinning, silvering or other surface coatings or patinas can be revealed by metallography. For example, chocolate-coloured coatings on a Renaissance bronze were shown to be of platinum, deposited by electrochemical replacement plating on bronze; gold coatings less than one micron thick were found on Moche metalwork, showing that gold had been deposited by electrochemical replacement gilding without the aid of a battery by the Moche; black-surfaced bronzes from ancient Egypt were produced by treating the surface of particular bronze alloys to create brown to black surface patinas; historic iron surfaces were treated by bower-barffing to deliberately oxidize the surface as a protective finish.

Broadly speaking, metallic corrosion is governed by three types of interactions: epitaxial, topotaxial or fractal, the latter often leading to chaos theory and random events dominating the corrosion, especially in the case of iron corrosion where there may be little remaining structural detail left. In copper alloys, the initial corrosion products are epitaxially deposited with the consequence that there is a good chance that retention of structural detail can be observed in a metallographic section. The initial corrosion product of copper alloys is usually cuprite or rarely tenorite, details of which are given in Table 6.1, and cuprite predominates as an initial corrosion product. Further detailed studies are given in Scott [58].

Depending on the environment in which the corrosive events concerning the metallic object took place, this cuprite may appear quite crystalline and deep red in colour, viewed under polarized light or in darkfield illumination (Chap. 3). Deep red cuprite crystals or intergrowths within the corroded metal itself are a good indication of the material authenticity of the object in question, and these features can

Table 6.1 Corrosion product of copper alloys

Mineral name	Formula	Crystal system	Colour	Mohs hardness
Cuprite	Cu_2O	Cubic	Submetallic red	3.5–4
Tenorite	CuO	Monoclinic	Metallic grey black	3.5
Spertiniite	$Cu(OH)_2$	Orthorhombic	Blue to blue green	1–2?
Malachite	$Cu_2(CO_3)(OH)_2$	Monoclinic	Pale green	3.5–4
Azurite	$Cu_3(CO_3)_2(OH)_2$	Monoclinic	Vitreous blue	3.5–4
Georgeite	$Cu_5^{2+}(CO_3)_3(OH)_4\cdot 6H_2O$	Monoclinic	Pale blue	?

readily be seen in the polished and unetched section of the object and are relied upon as an important indicator of authentic long-term burial. Etching tends to dissolve out these copper oxides or copper sulphides, which will either entail the regrinding of the sample followed by repolishing to retrieve the as-polished condition or very careful repolishing alone.

In some alloys or environments, yellow or yellow-red pleochroism manifests fine-grained or poorly crystalline cuprite, which either contains a fair amount of tin or zinc (Chap. 3), or has grown quickly, as in artificial patination systems often used to create inauthentic patinas on archaeological fakes. Different environments may also affect the extent to which the deep red colour of cuprite in cross section can occur.

As corrosion penetrates into an alloy, it may itself act as a natural etchant by attacking those regions more heavily stressed or corroding one phase preferentially. Figure 6.1 shows the section through a Bronze Age blade from Hungary, where the strain lines close to the surface are obvious, as corrosion has outlined them for us here (see also Fig. 3.9). Note that some of these grains of α_{Cu}-bronze have been eaten away entirely along the edge of this section.

Corrosion may create obscuring crusts with complex interlayers contiguous with the metallic surface, as shown in Fig. 6.2. Here the junction between the remaining metal of this Chinese bronze mirror of the Warring States period and the external corrosion can be seen.

There are essentially four zones of corrosion seen in this photomicrograph: the internal corrosion of the bronze alloy, a surface zone which is a discontinuity between the internal and external environment, and a thick external corrosion crust, whose outer later is composed of green corrosion products with occasional soil minerals. Note here the clear delineation between internal and external corrosion events. The view of the same section, under plane-polarized light at higher magnification, reveals something of the corrosive events at the original surface of the mirror (Fig. 6.3).

The Widmanstätten structure of the alpha + delta phases of the bronze continues to create an inhomogeneity in the corrosion crust close to the metal surface, and

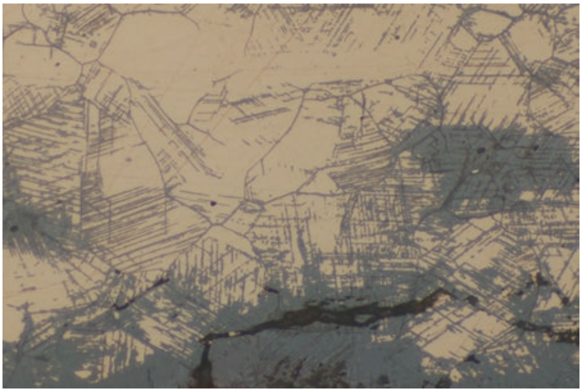


Fig. 6.1 Hungarian Bronze Age dagger blade section. The low-tin bronze has undergone extensive corrosion, with penetration along slip panes, some of which show perfect pseudomorphic preservation of microstructural detail. Unetched, magnification, x180

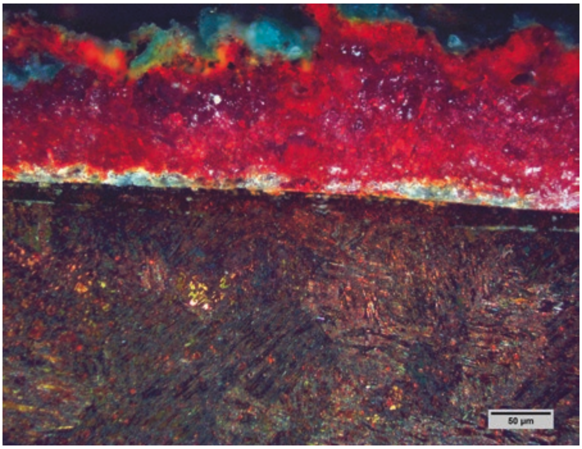


Fig. 6.2 Chinese bronze mirror from the Warring States with four different layers. The sound metal is on the left hand side, followed by a heavily corroded matrix, then a layer of redeposited copper, followed by the external corrosion crust. Unetched, polarized light, magnification x90

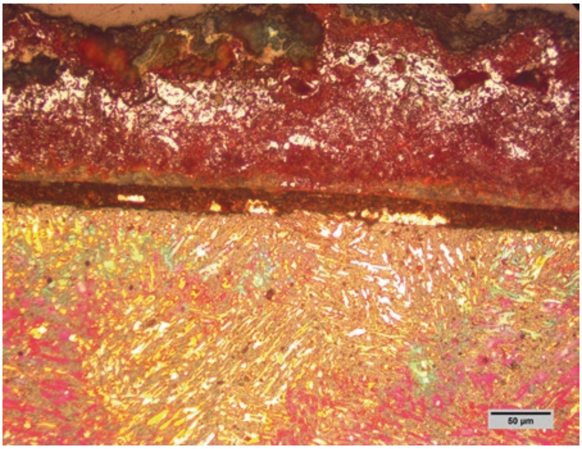


Fig. 6.3 Same bronze mirror as Fig. 6.2 viewed under polarized light with DIC. The Widmanstatten structure of the corroded interior is covered with a layer of redeposited copper along the surface of the original mirror external plane, and then to the left hand side, the corrosion crust covers the redeposited copper. Unetched, magnification x180

within the double boundary layer, copper has been deposited from solution during burial, resulting in the bright yellow phase seen in the photomicrograph of Fig. 6.2. The redeposition of copper from solution is a common event in the burial corrosion of Chinese bronzes and many others as well (see Bosi et al. [10]), and redeposited copper may be precipitated at surface boundaries or the original surface as Figs. 6.2 and 6.3 illustrate. The metallographer must be aware of these issues when interpreting the microstructure of ancient metals.

Dezincification is another type of de-alloying, which causes the selective removal of zinc from the alloy by the corrosion of the solid solution and the redeposition of copper as a porous layer. Stress corrosion cracking and dezincification are the most familiar forms of brass corrosion, and two types of dezincification are common: the plug and the layer type. The layer type is a uniform attack over the surfaces and is hardly documented for ancient single-phased brasses. The plug type can regularly be observed, but it is different to the intensive dezincification of modern yellow brasses, as single-phased α-brasses are less prone to dezincification than high zinc brasses. Brasses containing less than 15% of zinc have the same oxidation resistance as copper; therefore they are relatively immune to dezincification and impurities such as tin or arsenic increase the de-alloying resistance. Selective corrosion and de-alloying in ancient and historic brasses usually are metallurgically influenced and take place in localized areas after cold-work without sufficient annealing, as can be seen in Fig. 6.4, whereas drastic forms of dezincification can be perfectly studied in "antique" objects coming from the art market (see Schwab et al. [52]).

Pseudomorphic characteristics of particular phases may be preserved within the corrosion crust, and these can reveal structural detail near the surface. In ideal cases mineralized wood, textiles or other organic components are replaced with corrosion products and the micromorphology of these organic materials preserved within the corrosion crust, which can then be seen in cross section. The common forms of green-coloured alteration products of copper are shown in Table 6.2; for further

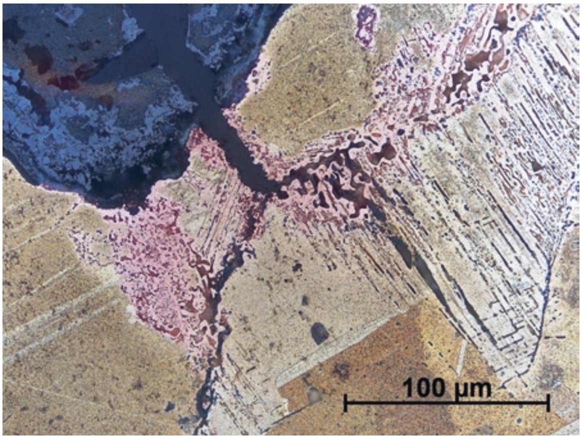


Fig. 6.4 Redeposited copper along corroded slip lines and stress corrosion cracks within a fulfilled groove on the surface of a Benin memorial head from the eighteenth century, which is made of leaded brass with 24% zinc. The head has never been buried, but the ornament has been enchased, and localized accelerated corrosion has been taken place by residual stress. Etched with acidified ferric chloride and viewed under bright-field illumination

Table 6.2 A tabulation of the important green-coloured copper and bronze corrosion products which are often encountered in corroded metallic sections. (After Scott [58])

Mineral name	Formula	Crystal system	Colour	Mohs hardness
Malachite	$CuCO_3 \cdot Cu(OH)_2$	Monoclinic	Pale green	3.5–4
Azurite	$2CuCO_3 \cdot Cu(OH)_2$	Monoclinic	Vitreous blue	3.5–4
Georgeite	$CuCO_3 \cdot Cu(OH)_2$	Monoclinic	Pale blue	?
Chalconatronite	$Na_2Cu(CO_3)_2 \cdot 3H_2O$	Monoclinic	Greenish blue	3–4
Rosasite	$(Cu,Zn)_2CO_3(OH)_2$	Monoclinic	Bluish green	4.5
Aurichalcite	$(Cu,Zn)_5(CO_3)_2(OH)_6$	Orthorhombic	Pearly pale green	1–2
Claraite	$(Cu,Zn)_3(CO_3)(OH)_4 \cdot 4H_2O$	Hexagonal	Translucent blue	2

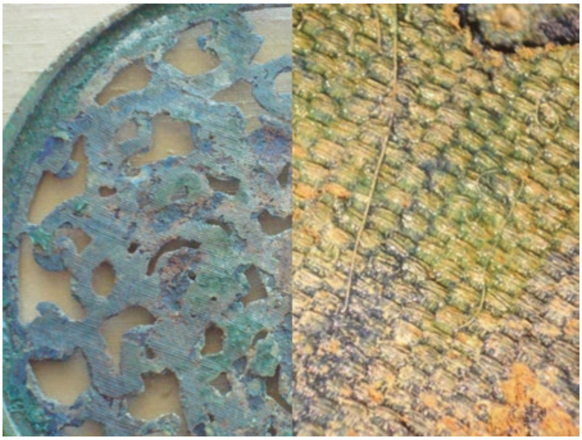


Fig. 6.5 Macroscopic view of the reverse side of the back of a Warring States mirror casing, showing the corrosion in cuprite and malachite which has preserved the traces of the textile interlayer. On the right hand side, at a magnification of x35, the silk textile pseudomorph can be seen in detail, entirely preserved in copper corrosion products

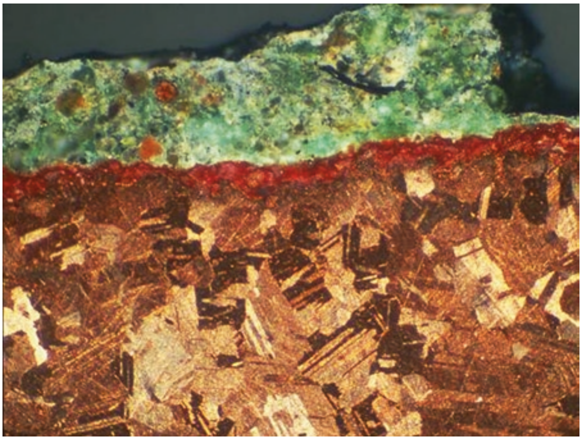


Fig. 6.6 One of five very important ancient Greek copper plaques which preserve a very early form of the Greek language. The lettering is entirely preserved in the malachite and copper trihydroxychloride corrosion products on the thick crust here, which overlies a thin, bright red cuprite layer, before passing into the worked and annealed copper grains of the sheet copper below. Lightly etched in ferric chloride, magnification x160

detailed information on all of these corrosion products and their characteristics, see Scott [58].

The preservation of pseudomorphic detail on the metallic surface, as shown in Fig. 6.5 from an ancient Chinese mirror of the Warring States period [62], is a mineral pseudomorph of an almost perfect silk textile used as an interlayer in the Chinese bronze mirror. No organic material remains, but the structure has been preserved completely in malachite and azurite corrosion products [60, 61].

In some cases, often very important, corrosion may have completely altered the metallic surface to a mass of corrosion products, which is the case of copper alloys, such as the section from the Greek copper plaque shown in Fig. 6.6. The plaque

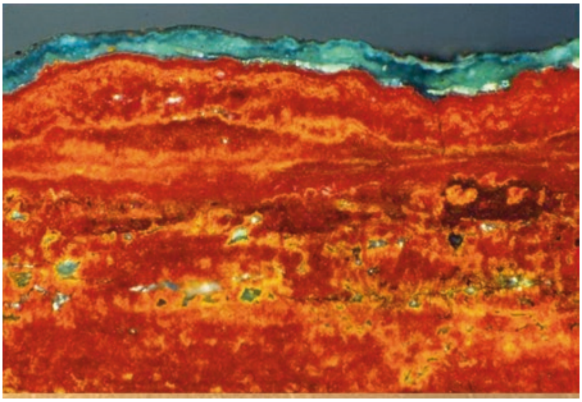


Fig. 6.7 Copper Dead Sea scrolls. Preserved lettering but completely mineralized copper sheet in this case, this preserves no metal whatever. Magnification x170

retains a surface in which letters can still actually be read, while the interior below the surface is covered with a complex corrosion crust [66]. Also the surfaces of the copper Dead Sea scrolls contain hammered lettering which can still be read [8, 58], while the matrix is completely converted to layers of cuprite which preserve little or nothing of the original metallic structure, as shown in Fig. 6.7.

There are many examples where the complete corrosion of archaeological metallic artefacts provides important structural information relating to corrosion events in the soil and how these impact the residual nature of the corroded matrix. A classic paper on the nature of the residual metallic matrix in the case of bronze alloys was that undertaken by Geilmann in [19]. Papers in which the nature of the corrosion can itself be used to link disparate museum artefacts together are exemplified by an example by Scott [56] on the examination of the patina and corrosion morphology of some Roman bronzes.

The Roman bronze statues of Togati, Roma and Venus (Demeter) and in the collection of the J. Paul Getty Museum were subject to a detailed technical study. Of particular interest are their unusual, mattes matte and finely preserved patinas, which closely parallel another bronze, the Nike, in the Cleveland Museum of Art. The bronzes, which date to AD 40–68, are described and analyzed, and an account of their corrosion is given, drawing on the work by Geilmann [19], who examined the corrosion of bronzes from sandy soils in Germany. The patinas of these objects contain substantial amounts of tin oxide and also display warty corrosion. It was postulated, and confirmed by analysis, that patinas of this kind should contain no chloride ions; thus, there are at least two types of warty corrosion of ancient bronzes. The first type, as here, is chemically stable and does not necessarily require strictly regulated humidity conditions. The second type of warty corrosion is related to the presence of chlorides, usually with an accumulation of cuprous chloride. The three bronzes studied here are closely related and are almost certainly from the same burial deposit, as evidenced by their associated soil and minerals. These materials were not completely cleaned from the surfaces of the bronzes, so essential information regarding their origin was preserved. Cleaning during conservation to a uniform "original surface" or "marker layer" would have removed this important evidence.

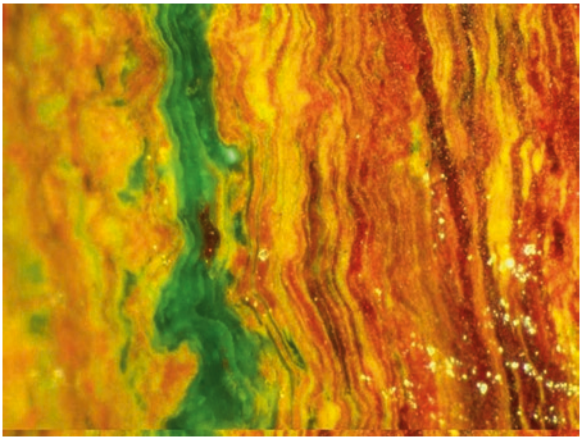


Fig. 6.8 Iranian toggle pin from the Middle Bronze Age, collection of Iran Bastan Museum, Iran. Total corrosion of the toggle pin has resulted in Liesegang rings in the corroded solid, which preserves no original microstructural detail. Unetched, magnification x 350

Robbiola and Portier [47] present a paper of wider significance which postulates a global approach to the authentication of ancient bronzes based on the characterization of the alloy-patina-environment system. Their work proposes a general framework for improving the practice of authentication of ancient bronze artefacts. It is shown that even if numerous technical and fundamental scientific improvements have overcome some of the limitations encountered in the characterization of materials, properties, metal and patina are always considered as independent systems. It is evidenced that authentication requires a global approach based on the investigation of the metallic materials-patina-close environment system. On this basis, the authors address the complex relationships between alloys, alteration (patinas) and environment (soil) and discuss the investigation of the consequence of decuprification (as a global phenomenon of bronze corrosion), taking into account the coupled interactions. An application from an example of a fake Chinese ding ritual vessel is then given.

The complete corrosion of some bronze artefacts creates complex layered structures which are caused by the slow interaction of corrosive solutions with the bronze alloy. Liesegang phenomena can then be observed in the corroded section if the growth features involve a determinative layered form as Fig. 6.8 illustrates.

6.1.1 *Deliberately Oxidized or Corroded Surfaces*

Oxidation techniques have been used to create surface films and colouration by light absorption, reflection or diffraction. A significant group of copper alloys, known in many different cultures of the Old World, was prepared by special patination techniques. In Egypt, the use of the black-patinated *hsmn km* alloy appears to be widespread, and Romans took the knowledge of the technique and applied it to produce the so-called Corinthian bronzes, which are known in Bronze Age Greek as kyanos and as *shakudo* in Japan from the twelfth century onwards [16, 39]. Most of these alloys contain up to several percentages of gold and are combined with inlays of gold, silver or electrum [16, 41].

The black colour of these copper alloys is essentially an altered cuprite with some tenorite in which gold particles are finely dispersed and the lustrous black blue surface is mainly due to light absorption and diffuse reflection by the fine gold particles [39, 41]. Rare examples of this technique from the European Bronze Age are exclusively made of nearly pure copper, which were also black or dark brown in surface colouration, sometimes combined with gold inlays [5, 6, 53]. The analytical study of the Egyptian bronzes by La Niece and co-workers [33] showed that they were originally intended to be polychrome. Not only were the eyes, brows and nipples of some figures coloured but also regalia, clothing and jewellery. The range of materials and techniques included the well-known precious metal, glass and mineral inlays, as well as coloured alloys, patinated metal and applied pigments. Inlays may also have been patinated, particularly those produced in an arsenical copper alloy.

A range of other alloys were also employed using copper-silver alloys, *shibuichi*; *kuromido*, arsenic-copper alloy; *santoku*, a leaded tin bronze; and *shintyuu*, a leaded brass. These alloys could be used to create a whole range of colours including grey, grey-green and ranging from light to dark olive and earth browns. Imitation of Japanese alloys of *shakudo* or *shibuichi*, of long antiquity, led to a fashion for oxidized silver in France by the 1840s, and the fashion for oxidized silver surfaces continued up to the First World War [48].

Another technique employing oxidation to create blackened surfaces in high zinc alloys containing a small amount of copper was from ancient India, known as Bidriware. Analysis shows that the maximum copper content of such alloys was 10% but usually less than 5% with some lead [29, 31, 32]. The objects were cast and inlaid with silver, gold or brass. The final stage in the production of the black surface on the alloy is the use of a special local earth and ammonium chloride [31]. The earth is recommended to be taken from old palace walls and associated areas which are likely to be rich in the decayed products of urine, and therefore these agents are thought to be active in producing the blackened surface of the Bidriware but leaving the inlays unaffected [29].

Iron surfaces could be coloured by heating or chemically producing oxide layers appearing blue, brown or black in dependence of their thickness [67]. They can also be blackened by forcing a layer of flash rusting, followed by treatment with hydrogen gas to produce black velvet-like surfaces, referred to as bower-barffing [21].

6.2 Plating

6.2.1 Gilding

There is a progression in terms of surface coatings from the base metal to the overlying coating. For example, iron objects can be coated with copper, copper alloys with silver, silver with gold and gold with platinum. There are even examples of lead beads from the La Tolita culture of lead overlaid or inlaid with pieces of platinum [60, 61]. Gilding has probably been one of the most widespread plating technologies all over the ancient world. Gilding was applied to imitate solid gold, as a rare and valuable metal, and there are many cultures over the ancient world where gold coatings have been made, both over copper and silver alloys and, later, also over iron.

The early use of foil or leaf gilding may have involved a mechanical rather than metallurgical process, and examples are known from the beginning of the third millennium BC of silver nails covered with gold leaf from Tell Brak in Syria and of copper nails from Abu Shahrain, Iraq, from circa 2500 BC [42, p. 172; 43, p. 2]. Mechanical fixing or inlay techniques have been exclusively used in the Old World during the Bronze Age, and the technique has remained a common practice in all cultures up to modern times. An example from a tenth century AD context can be seen in a nose ornament from Ecuador in Fig. 6.9.

A real innovation and the first metallurgical gilding process is diffusion gilding, also called diffusion bonding, which is best known for gold and silver. Diffusion bonding has been first evidenced for an Elamite roundel from Iran, which is dated to the fourteenth/thirteenth century BC [42, p. 176; 43], but the technology must have been already well known at this time, as around one-third of the analyzed gold

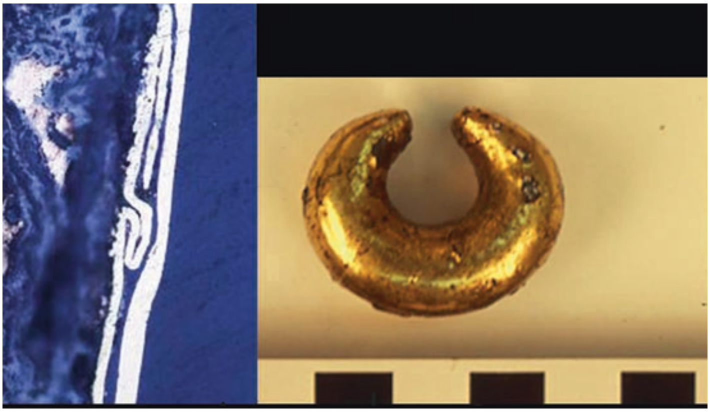


Fig. 6.9 Foil-gilded penannular nose ornament from the site of La Compania, Los Rios Province, Ecuador, from the tenth century AD secondary chimney urn burial. The section through part of the surface shows corroded copper beneath a typical gold foil covering where folds can be seen in the foil. Unetched, magnification on left is x75. Scale bar on the right is in centimetres

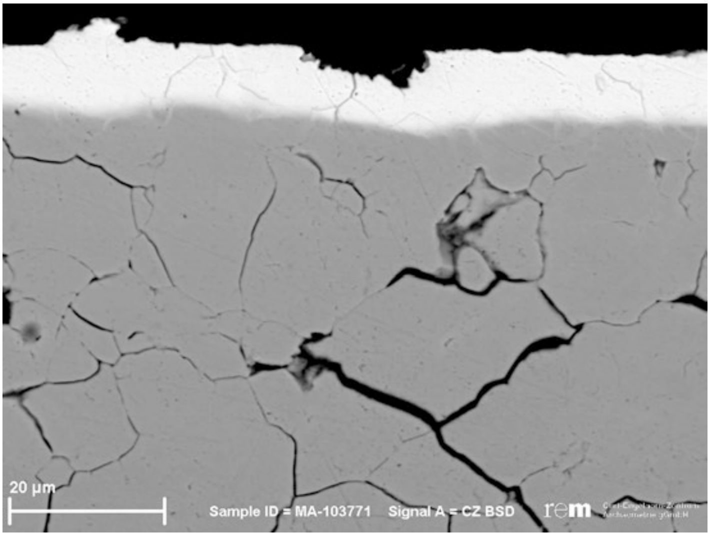
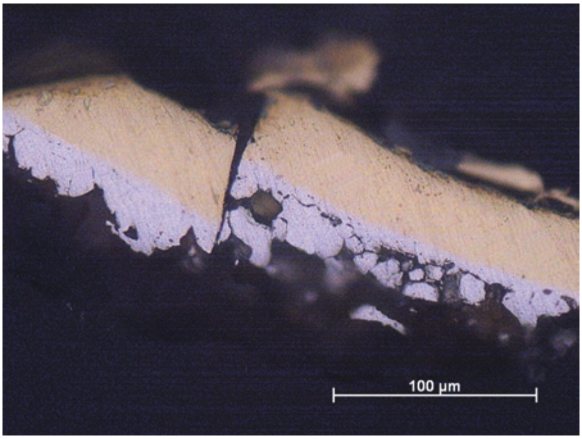


Fig. 6.10 SEM-BSE image of the intergranular fractured microstructure of a decorated silver quiver from the Royal tomb of Qatna in Syria shows a thin layer of gold, which is bond to the silver substrate by diffusion

Fig. 6.11 Micrograph of the gilded silver foil from the head of a bronze rivet from the tomb of Asperg »Grafenbühl«, Germany, dated to around 500 BC



items from the Royal tomb of Qatna in Syria, dated to the early fourteenth century BC, are in fact gilded silver, as can be seen in Fig. 6.10.

Diffusion gilding is best documented for Greek and Etruscan items since the eighth/seventh century BC and must have entered Northern and Western Europe during the sixth century BC, when first examples can be proven (Fig. 6.11). Diffusion gilding has also been practised in Southeast Asia [49] and in South America.

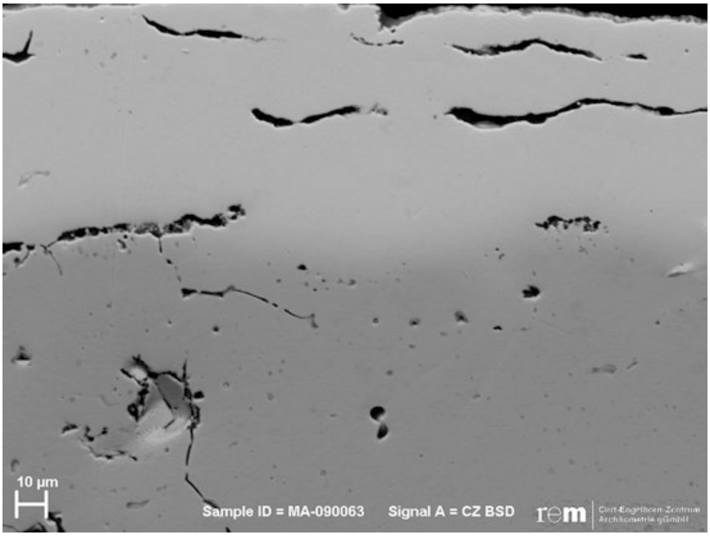


Fig. 6.12 SEM-BSE image of a foil and subsequent fusion-gilded silver spiral ring fragment from burial 4 in Prohear, Cambodia, dated to 44 BC to 51 AD, showing three superimposed gold layers and the zones of interdiffusion which are disrupted by cuprite inclusions and cavities

The clamping together of gold foil or gold leaf and silver to anneal the couple easily creates a diffusion bond between surface and substrate, as both metals are totally soluble in each other (Chap. 4). Since the diffusion coefficient D_{Ag} is greater than D_{Au}, the Kirkendall effect emerges by volume expansions on the slower diffusion component side which induce surface contour changes, optically evident through bubbles, which are significant for diffusion-bonded objects ([50, 59]). The micrographs of the cross section of diffusion-bonded items usually show strong bonded layers without any gaps, and an EDX line scans or element maps show the gradually decreasing gold and the increasing silver contents from the attached gold to the silver layer on the inside (see Schorer et al. [51], p. 206). The presence of copper can form copper oxide inclusions by inner oxidation, which locally prevent the bonding, as shown in Fig. 6.12.

Another important metallurgical technique is amalgam or fire gilding. Gold can be mixed with mercury to create a series of pasty amalgams. It was recognized early on that if a pasty mass of gold amalgam was spread over the surface of cleaned copper, and gently heated, that interdiffusion of mercury between the substrate and the gold layer would ensure a metallurgical bond [42]. Most of the mercury evaporates leaving a dull and porous surface, which must be rubbed and smoothed. The spongy gold surface of fire-gilded objects can often be seen in cross section shown in Fig. 6.13, especially in depressions, and is quite distinctive.

Amalgam gilding creates gold-mercury intermetallic phases, and traces of mercury can usually be detected by XRF analysis from the surface of such objects. The mercury amalgam technique came to dominate the gilding used in historic periods,

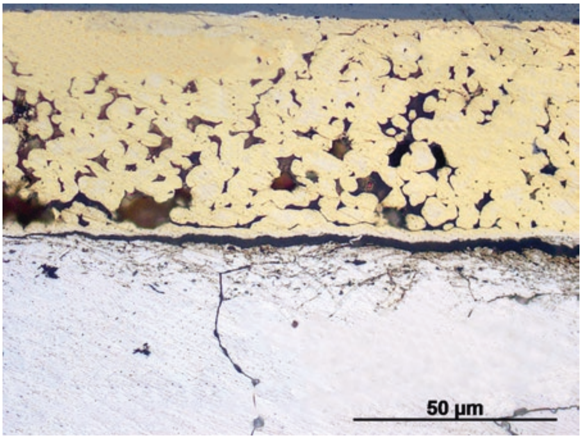


Fig. 6.13 A silver falcon brooch from the early medieval cemetery from Bedburg-Königshoven in the Rhineland, Germany, has a typical thick porous fire-gilded surface

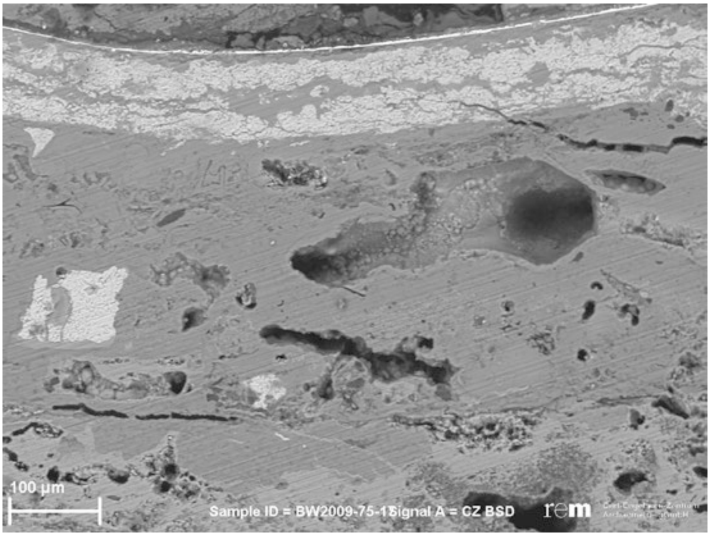


Fig. 6.14 SEM-BSE image shows the corroded iron disc of a cameo fibula from Mannheim-Seckenheim, dated to the early nineth century AD. The iron has been plated with a layer of copper and then fire gilded

but leaf and diffusion bonding were still extensively used. Mercury amalgam gilding probably originated in China, during the Warring States period [42, 43]. By the second century AD in the Old World, mercury amalgams were commonly used, but these were used surprisingly early in the Celtic world where knowledge of the technique goes back to the first century BC [22, p. 255; 34, 43]. Some rare earlier examples could indicate that amalgam gilding was known in Europe before this period (see Kallfass et al. [28]; Oddy [42]), if their dates are secure. Fire gilding of iron was also employed, as can be seen in Fig. 6.14.

Bronze Age fire-gilded objects such as a disc from Rathgall in Ireland and the metal-hilted sword recovered from the river Niers near Oedt in Westphalia (Germany) have been proven to be fakes or incorrectly dated (Craddock, personal communication; [54]). Certain regions of the ancient world, such as the entire continent of pre-Hispanic South America, never used amalgam gilding.

Yet another technique of surface treatment was reported for the first time by Bergsøe, following his examination of a number of gilded copper objects from the Esmeraldas-Tumaco area [11]. Some of the fish-hooks and needles from this area appear to have been made in a tumbaga alloy, followed by depletion gilding, but examination by Bergsøe of successive surface scrapings convinced him that the gradual decrease in gold content towards the centre of the object was a consequence of a fusion-gilding process, in which a piece of shaped copper was dipped into a molten gold-copper alloy. After dissolving the copper base of five gilded objects in dilute nitric acid, Bergsøe found the remaining scales to have a composition of 64.8% gold, 26.8% copper and 8.24% silver, an alloy with a liquidus of about 970 °C. The copper-base alloy averages a gold content of 2.1%, perhaps as a result of contamination or as a result of the reuse of scrap. Work by Scott [55] confirmed the existence of wash-gilded copper from both the Esmeraldas-Tumaco and Nariño areas. An example is shown in Fig. 6.15, which is a cross section through a fusion-gilded fish-hook from La Tolita. The thickness of the coating here is 180 microns and has been made in a gold-copper alloy of composition 26% gold, 2% silver and 72% copper.

There is a zone of interdiffusion of 35 microns. The liquidus temperature of the coating is 1080 °C, while the melting point of the copper base is 1100 °C. A delicate metallurgical operation must be conducted in order to affect this kind of surface coating. The porosity close to the underlying surface of the copper shows a series of pores which may be due to the Kirkendall shift, as the rate of diffusion of gold in copper is greater than the rate of diffusion of copper in gold. This can have the effect of creating porosity as the boundary as gold diffusion proceeds.

Gilding, mise en couleur, surface enrichment, depletion gilding and colouring are all used in various ways in the literature to describe the same event: the removal of

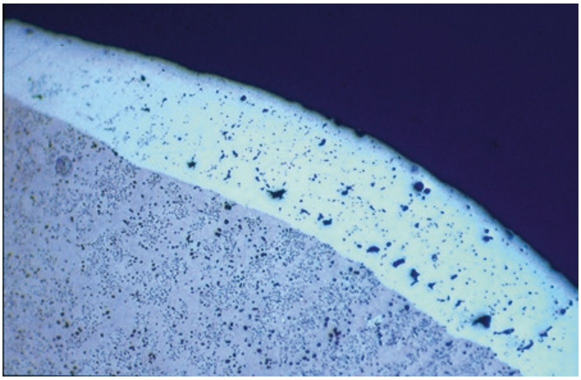


Fig. 6.15 Diffusion-bonded gold-copper alloy fusion coat over copper. Fish-hook from the site of La Tolita, Ecuador. A tour de force of diffusion bonding on a small object no more than 1.6 mm in diameter. Etched in ferric chloride, magnification x130

one or more constituents from a gold alloy to leave a surface enriched in gold which, on subsequent burnishing, gives the appearance that the whole object (or selected parts of the object) is golden in colour. The number of these descriptive terms used in various contexts has led to some confusion in the archaeological literature as to how they are to be applied. Lechtman [35] prefers the term depletion gilding to surface enrichment; she defines it as "The enrichment of a surface in gold by the removal of other alloying elements already present". Gold is a noble metal and highly resistant to corrosion in soils and atmospheres, because of its low chemical affinity for most elements and its high positive electrode potential. Gold alloys become increasingly susceptible to corrosion as the content of the less noble constituents rises. Tammann [69] found that the resistance of gold alloys to tarnish and corrosion at room temperature was not greatly affected, as long as the gold content of the resulting alloy was not below 50 atomic percentages (about 65 wt. %). For a general review, see Rapson and Groenewald [46]. Depletion gilding is a corrosion process, which is termed de-alloying in modern corrosion sciences. De-alloying is an electrochemical reaction that causes surface depletion effects in gold alloys by the selective dissolution of copper and silver from the solid solution leaving behind a porous residue of pure gold [14]. Due to the differences in the standard electrode potentials of silver and copper to gold, they dissolve anodically in most moist environments, and silver can also be removed by the reactivity of the halogens towards silver.

In contrast to other well-known de-alloying systems such as copper-zinc, there is no dissolution-redeposition mechanism, as gold usually does not undergo dissolution [14]. One would expect that the enrichment of gold on the surface could stop the corrosive attack, but further diffusion of the more reactive elements towards the surface and the gold away from the surface is proposed for the continuing of the leaching process [14, 18]. As surface alloying element's atoms were dissolved, the residual gold atoms reform into gold-rich islands so that fresh atoms were exposed layer by layer. As the corrosion proceeds, the surface reorders by island nucleation and growth; finally the islands grow into an interconnected structure resulting in a very thin epitaxial surface coating of gold. A typical island-and-channel morphology in the cross section of a tumbaga alloy from the Tairona area of Colombia reveals the general pattern of attack. The weak plant acids are able to continue their attack and alteration of the surface as the gold atoms rearrange themselves to create the channels seen in the photomicrograph below in Fig. 6.16.

The compositional contrast of the microstructure of a silver and gold alloy from Prohear in Cambodia clearly reveals the enrichment of gold along the channels (Fig. 6.17).

Surface enrichment techniques have been extensively used in ancient South America to change the surface composition of gold-copper or gold-silver-copper alloys [57]. This is especially so in Colombia where the great majority of metalwork was made in copper-gold alloys and there is ethnohistorical evidence for this kind of surface alteration as, for example, Fernández de Enciso, writing in 1519 of the Indians of Santa Marta, Department of Magdalena, an area of the Tairona culture: "…there is in possession of the Indians much gold and copper. There is also found much gilded copper. The Indians say that they gild the copper with a herb which is

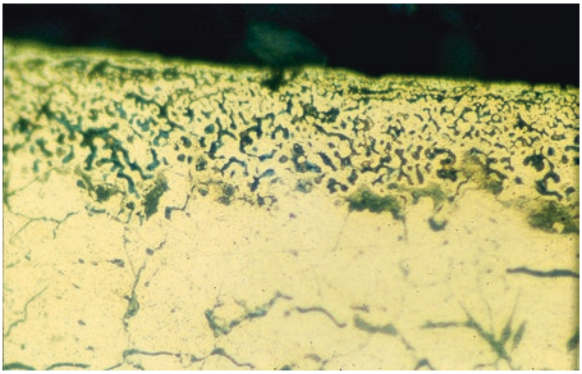


Fig. 6.16 Surface enrichment in gold has created this island and channel morphology in an ancient Colombian gold alloy from the Nariño area. The gold content at the surface rises to about 75–80%, while the bulk of the copper-gold-silver alloy has about 25% gold, 70% copper and 5% silver

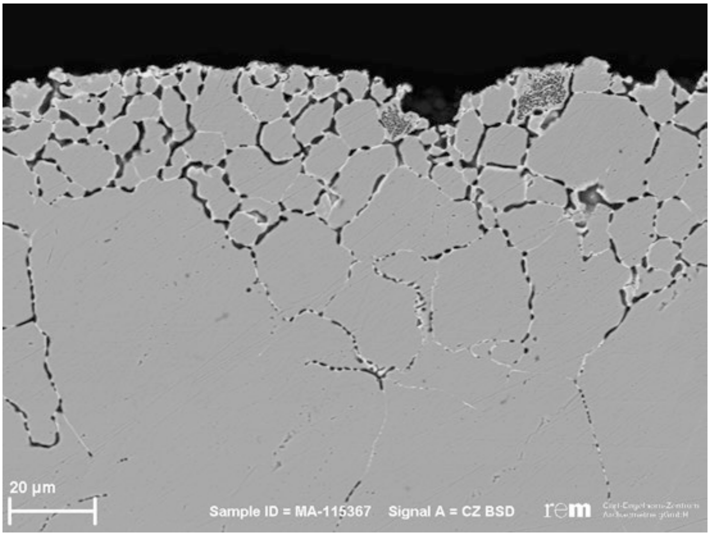


Fig. 6.17 Depleted surface of a spiral made of a silver and gold alloy with 63.5% silver and 36% gold from Prohear, Cambodia

in that land, crushed, and with the top taken off; and they wash the copper with it; and placed in the fire it assumes the colour of very fine gold, and changes in colour more or less according to whether they give it more or less of the herb…”.

Depletion gilding is rarely documented for the Near East [43], but some examples are known from Southeast Asia [49], and evidence from England and from northwest France for the late Iron Age suggests deliberate surface treatment by goldsmiths to enhance the colour of the alloys [22, 34].

Electrochemical deposition of gold films from solution was reported by Lechtman [36] used as the gilding of some Moche period metalwork (0 AD–600 AD), from the site of Loma Negra, near the Peruvian-Ecuadorian border. Examination showed them to be of copper with very thin gold coatings of 0.5–2.0 micron thickness. The coatings were relatively uniform and covered all surfaces, and there was a solid-

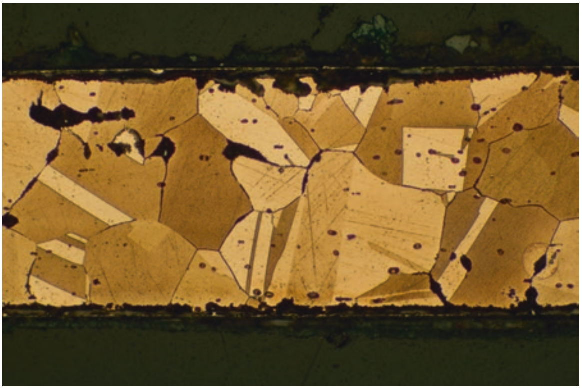


Fig. 6.18 Electrochemically plated Vicus disc from ancient Peru. The underlying copper has a trace of gold content, but the thin, continuous gold covering can just be seen at this magnification. Etched in ferric chloride, magnification x80

state diffusion zone between the gold and copper showing that, at some stage, heating was carried out. There was no evidence of mercury gilding or the use of gold foil or leaf or of the flushing-on of molten gold. Lechtman suggested the use of an electrochemical replacement technique: identical coatings were produced in the laboratory using gold dissolved in aqueous solutions of $NaCl + KNO_3 + K_2SO_4 \bullet Al_2(SO_4)_3 \bullet 12H_2O$. Gold can go into solution in this aqueous mixture in the form of the complex $[AuCl_4^{-}H^{+}] \bullet 3H_2O$. Sodium bicarbonate additions were made to bring the pH up to 9. Under these conditions cleaned copper sheet placed into the simmering solution became plated with gold. By dissolving silver in the same solution, it is possible to produce silver-plated copper. An example of an electrochemically plated ancient Peruvian dangle from the Vicus culture is shown in Fig. 6.18.

The electrochemical replacement technology has been reported exclusively from Peru and Ecuador for the early centuries AD so far [25, 57] and is a remarkable metallurgical achievement by the ancient pre-Hispanic cultures, at a time when the Western world had no knowledge of the procedure at all.

6.2.2 *Silvering*

The existence of silver-enriched copper-silver alloys is common. Fusion of silver or silver-copper alloys to the surface has been extensively employed in the Old World, especially by the Romans to fabricate silver-plated coins or decorative items [30, 70]. Where the base alloy was of copper, a layer of solder of a silver-copper alloy could be flowed over the surface, creating a eutectic alloy at the join. If the core was of iron, this soldering or fusion process could not be used, and the silver plating had to be carried out either by using a separate silver-copper hard solder or by soldering silver foil to the iron surface. Silver sheets were also soldered to copper alloys (Chap. 4).

In the binary alloy, the working and annealing to shape create copper oxidation (this also applies to copper-rich tumbagas), and the removal of scale and cleaning of

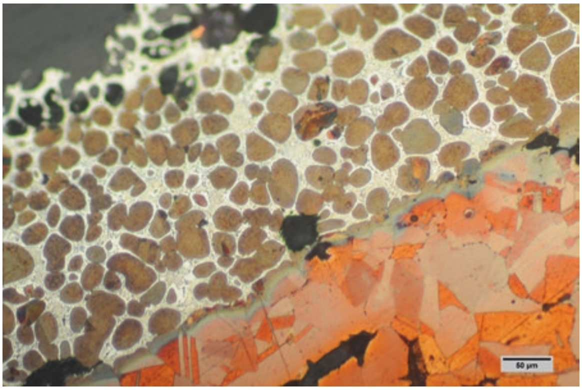


Fig. 6.19 Silvered penannular nose ornament from La Compania, Los Rios Province, Ecuador, from secondary chimney urn burial, the tenth century AD. Section shows the skilful, thick silver-copper alloy coating over the copper nose ring, which is then surface enriched in silver by depletion of copper, so that the entire nose ornament appears to be made in silver. Etched in potassium dichromate followed by colour etching to reveal the worked and annealed copper grains, magnification given on scale bar is 50 microns

the surface create a surface-enriched effect. It would not be necessary to employ the ferric salt and sodium chloride mixture in the surface treatment of these copper-silver alloys, since copper removal is all that is required. In the New World, silver-copper alloys are mainly found along the pacific littoral from Ecuador to Peru and in the Andean highlands (Meggers [38], pp. 133–8, 152, 163). They are also found in the Nariño area of Colombia.

These alloy surface alteration techniques employing silver can be very hard to characterize if metallographic examination cannot be carried out. An example is shown in Fig. 6.19, which is the cross section of a penannular silver nose ornament from Ecuador. Surface study with X-rays would only reveal a silver-copper alloy, as the coating is 100 microns thick. Metallographic examination shows that under the silver-copper alloy layer, which has been fusion-silvered to the surface, there is a pure copper interior which has been hammered and worked to shape the nose ornament before the silver-copper alloy of lower melting point was fused or flowed over the surface. This silver-copper alloy was then lightly worked and annealed, since some annealing twins can be seen in the alloy coating, and was then enriched in silver by pickling to clean and remove some of the copper from this binary alloy.

Silver plating on iron is much less common, but with introduction of coinage, iron-cored coin forgeries so-called *subferrati* appeared, which were coated with more valuable metals like silver [1, 70].

6.2.3 Platinum Coatings

The only culture of the ancient world to make use of platinum coatings was that of the Esmeralda-La Tolita Indians, along the Pacific littoral of Ecuador and Colombia [55, 60, 61]. Metallographic examination, shown in two examples below, reveals that two different techniques of platinum coating were employed. In one, shown on the upper section, a thin layer of platinum grains was applied to the surface and then heated with the blowpipe, slowly creating an interdiffusion zone between the unmelted platinum grains and the gold substrate. On burnishing, the platinum alloy surface (isoferroplatinum, as the platinum usually contains a small percentage of iron), will assume an interesting range of platinum colours, which in burial may be tinged with a slight blush of iron corrosion in the form of haematite. An example is shown in Fig. 6.20.

In the second type of platinum coating, a thin diffusion-bonded sheet of gold-platinum sintered alloy is made, which is then hammered and annealed to create a composite thin sheet. This gold-platinum sheet or foil is then hammered over the gold substrate and adhered by diffusion bonding. Metallography reveals this truly remarkable achievement of the La Tolita Indians. Figure 6.21 is from a small armlet or bangle in the collections of the National Museum of the American Indian, Washington, from La Tolita, which is part of a bimetallic finish used on this particular object. Here a layer of gold appears to have been applied to a gold-platinum sintered sheet beneath. The bimetallic finish is used in this object to create contrasting surface design in gold and gold-platinum.

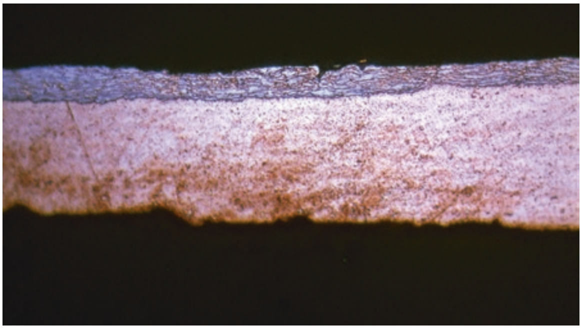


Fig. 6.20 Sophisticated platinum-plating technology from the Indians of La Tolita, Ecuador, from about 100 BC to early centuries AD. Here a separate, well-hammered gold-platinum composite foil has been made, and this foil is then diffusion bonded to the gold sheet beneath to make a platinum coating of some thickness. The silver content of the platinum-gold composite is not the same as the silver content of the gold sheet beneath, showing the separate origin of the two components. Etched in aqua regia, magnification x80

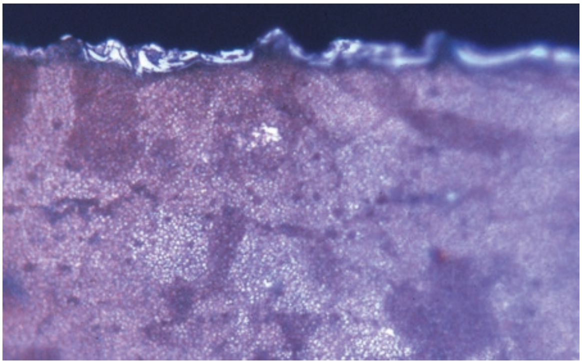
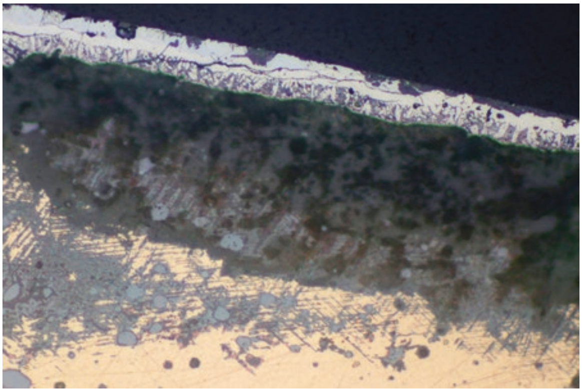


Fig. 6.21 Platinum plated dangle from La Tolita. Here tiny platinum laths have been applied to the surface of the finished object and then carefully heated with the blowpipe to create some interdiffusion. The platinum-iron native alloy produces a steel-grey surface colouration. Etched in aqua regia, magnification x680

Fig. 6.22 Tinning on a Chinese belt buckle from the Tang Dynasty. The three layers of tinning which have formed by diffusion can just be seen, from small remnants of metallic tin to the eta phase and then the epsilon phase and the alpha + delta eutectoid phase. Unetched, magnification x240



6.2.4 *Tinning*

The history and technology of tinning copper alloys has been well described by Meeks [37], which should be consulted for detailed information. Tinning has been used to produce high-reflecting and corrosion-resistant surfaces, because tin is non-toxic, has a pleasant appearance and is a cheaper alternative to silvering. Tinning produces very thin layers and has also been used to imitate silver in coin forgeries [30]. Tin is usually applied in the liquid state, due to its low melting point, and therefore forms phases with the substrate alloy by solid-state diffusion [37]. Excess tin is rarely found on the surface of tinned copper alloys, but all the intermetallic compounds η, ε and δ, as well as the eutectoid, are (Fig. 6.22). The η-phase Cu_6Sn_5 is common. Surface layers of eutectoid can also form by inverse segregation; either an accident of casting or deliberately encouraged by manipulation of the casting conditions has been responsible for tin-enriched surfaces on Bronze Age implements and Chinese artefacts and has generated a considerable literature. In order to investigate these surface alterations in detail, metallography is essential.

The tinning of iron is principally a protective coating; as unalloyed iron and steel readily stains and rusts, it has to be coated or serviced. While blades have to be consistently polished and oiled, wrought irons have usually been black annealed or coated.

6.2.5 Copper Plating on Iron

Copper alloy plating on iron is a particular technology from the Iron Age to modern times, and a number of techniques had been evolved (see Ankner and Hummel [2]; Corfield [15]). The first method involves the use of a sheet copper metal, which is wrapped around the iron leaving flanges which are then tightly held together by striking from either side or just fixed into a notch [40]. The copper plating could also be applied by hammering on to the prepared surface of the iron which could be roughened to form a physical bond with the plated surface. This technique has widely been applied in Europe for the substantial plating of silver and copper alloys on the base terminals of belt fittings, stirrups or sword hilts from the early medieval to high medieval period. It is also possible to apply copper alloys simply by dipping the iron object into a molten copper alloy, but fusion plating of copper alloys was widely used for practical reasons. The technique has been actually described by Theophilus as part of the manufacturing process of barrel padlocks: “Now make an alloy of two parts of copper and a third of tin and crush it to a powder with a hammer in an iron pot; then burn some gold, add a little salt to it, mix it with water, smear it all around and sprinkle the powder around it. When it is dry, smear the mixture around it again more thickly and put it on live coals. Then carefully cover it all around with charcoal let it cool by itself and wash it and this way you can braze anything of iron that you want but it cannot be gilded in any other way” [24]. Corfield [15] has pointed out the improvement of protection against corrosion, but the joining by brazing seems to be much more relevant, as mostly small and thin pieces are joined, which are difficult to forge weld, because of the fast overheating and the high burn-off. In the early Iron Age, these joins, induced by technological reasons, were skilfully used for individual decorative plating [17], but later on the brazing alloys were adopted to cover the hole object in the most cases (see Ankner and Hummel [2]; Corfield [15]).

Figure 6.23 shows a sample from some unspecified rings from Assur, which are ostensibly copper plated, but most probably just brazed to join the parts together. Plating iron with copper alloys might also have an economical background to save the higher-prized metal. Early examples are bronze-plated iron bowls from Voulokaliva near Halos in Greece, dated to the end of the ninth and the beginning of

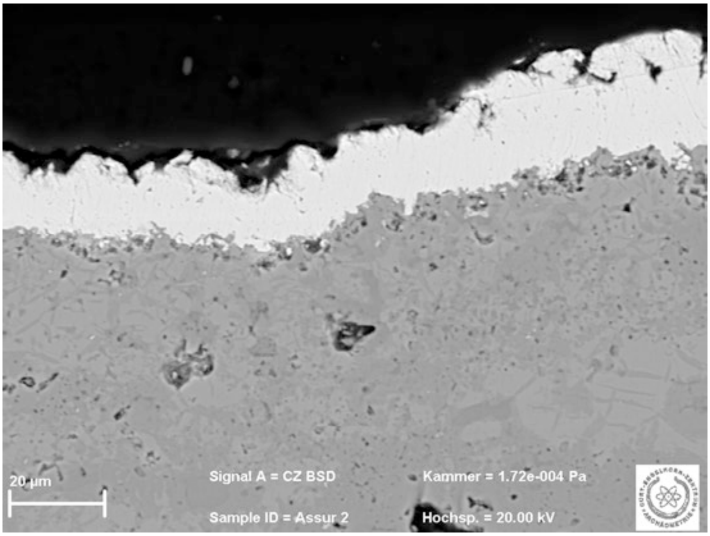


Fig. 6.23 SEM-BSE image of a cross section from an iron ring from Assur. A layer of copper covers the whole surface and has fulfilled all cavities

the seventh century BC [3], but like silver, copper-plated iron-cored coins had been produced to imitate real copper-alloyed coins (e.g. Haubner and Strobl [23]).

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