# Chapter 4
# Metallography and Microstructure of Metallic Artifacts

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## What is Metallography?

Metallography is the application of microscopic techniques to sections or polished surfaces of ancient metallic materials for the purpose of gaining information concerning composition, microstructural components, extent of corrosion, or method of fabrication. Metallography was first applied to archaeological materials in the early decades of the twentieth century and has been of use to archaeologists ever since. Comparatively few metallographic studies were published between the World Wars, although the impact of such studies on archaeology became apparent in the 1940s–1960s through the publications of prominent scholars such as H. H. Coghlan at the Borough Museum, Newbury, Berkshire, and, later, Cyril Stanley Smith at Massachusetts Institute of Technology (M.I.T).

Metallography can help to inform us about the use and value of metallic materials in the past as well as aspects of their extraction from ore and subsequent fabrication into finished artifacts. The primary distinction to be made in a great number of initial studies concerns whether the metal or alloy has been cast to shape, or whether it has been worked and annealed to shape. Often, artifacts are selectively worked by hammering to harden them. This kind of evidence may demonstrate technological and sociocultural differences between metalworkers and metal-using societies as they relate to production practices.

Metal objects may be plated or coated with other metals, which limits the extent to which nondestructive analysis can be used to provide definitive answers. For example, precious metal alloys such as silver–copper and gold–copper alloys are often finished by surface-enrichment depletion gilding, or some other form of surface treatment. In such cases, metallography provides further information and can determine, in

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conjunction with chemical analyses of the polished cross section, the technique used to create the surface coating (see below).

Metallographic studies of early copper artifacts show more than just how objects were shaped and worked. Such research is also the only way to really prove the use of native (naturally occurring) copper instead of copper that was smelted from ores. The transition from native to smelted metal marks an important stage in early metallurgical development. Thus, metallography is an essential tool for answering questions about the origins of complex metallurgy.

One of the most important applications of metallography is to ancient ferrous materials. In Southwest Asia, the earliest iron artifacts were made from native (i.e., meteoritic) iron and later by the bloomery process in which the iron was never really molten. With metallography, the researcher can determine whether the artifact is made of native iron, whether it has been made of a number of pieces forged together, whether the cutting edges have been quenched to harden them, or whether the artifact is made of wrought iron from a bloomery process or a low-carbon steel. In China, early ferrous materials were often made in cast iron; softer tools and weapons could be fabricated by decarburizing white cast iron. Information relating to these developments and the utilization of particular materials must be obtained by metallography.

Finally, numerous questions relating to the authenticity of ancient metallic artifacts, particularly silver and bronze artifacts from uncertain contexts, can be answered through metallographic methods in combination with elemental and isotopic data. In cases of authenticity, it is often possible to adduce enough information from the metallographic section to avoid the need for further studies. This is particularly true in the case of ancient bronzes, where the extent of patina (corrosion) penetration and the type of patina may be sufficient evidence to condemn the artifact as a modern reproduction.

## Sampling and Interpretation

Usually, a small sample has to be taken from the object under study in order to carry out the metallographic examination. The artifact is often sampled by cutting a small section with a jeweler's saw and the resulting sample is then embedded in a suitable mounting medium, such as Buehler© epoxide resin in a 1- or 1.25-in. diameter casting mould. The orientation of the sample in the mould should be carefully noted, as different metallurgical or microstructural detail may be seen in a transverse (or "cross-") section as compared with a lateral section. The mounted sample is then ground and polished using wet silicon carbide papers and diamond powder suspension in water. When mounted samples are studied, the surface of the metallic specimen should be examined first in the freshly polished state, followed by etching with a suitable chemical reagent to draw out specific features in the metallic structure through 'selective corrosion'. In some etching techniques, there is no selective corrosion, but differential deposition of a complex chemical film on the surface of the sample, as in color or tint etching. In samples where the interface between the original corrosion crust and the metal must be examined, it is important to study them in the polished condition only. Etching may attack the corrosion crust even as it reveals the metallic structure.

Examination of the polished section can utilize a number of scientific methods that each provides different types of information. The reflected light microscope (or metallograph) is the most common (and cheapest) method and can be used to determine manufacturing techniques, degree of corrosion, and questions of authenticity. The samples can also be placed in an electron microprobe (electron probe microanalyzer, EMPA), scanning electron microscope (SEM), or studied with X-ray fluorescence (XRF) techniques. All of these analytical methods provide information about the composition of the metal and, more indirectly, about the methods employed for the production of the metal(s) used to make that object (e.g., ore types, firing temperatures, and alloying).

It is possible with large objects, or with the edges of coins, to polish selected areas of objects in order to examine the metallographic structure *in situ*, in cases where it may be impossible to cut or remove a section from the object. Microstructural features may be selectively etched or preserved in corrosion on metallic surfaces, which allows this technique to reveal micromorphology directly. One should remember that a polished section is a two-dimensional view of a three-dimensional structure and is only a small part of a larger (and internally heterogeneous) artifact. Thus, supplementary techniques such as X-radiography can be employed to reveal the internal structure of the entire object.

There are often severe restrictions on the quantity of metal which can be removed from an artifact for metallographic examination, especially non-ferrous metalwork. On the other hand, even a very small sample (smaller than a pinhead) can be mounted and polished for examination, although great care has to be exercised at all stages of preparation if samples are that small. It is obviously much easier to work with larger samples although, by archaeological standards, samples the size of a pea can be considered ‘large’, unless whole artifacts or substantial fragments are available for sectioning.

There are a number of criteria that should be considered before any sampling is undertaken:

1. What questions are you trying to answer with metallography? The nature of the questions determines where you sample the artifact, how you mount the sample in resin, and how you analyze the mounted section.
2. The microstructure of the samples should not be altered in the process of removal. Thus, excessive heat or physical deformation of the object during sampling should be avoided at all costs, as it will change the interpretation of the artifact.
3. The sample should be representative of the object as a whole, or should be selected to study a particular feature or area of the object.
4. The location and orientation of the sample (in its dimensional relationship to the artifact) should be marked on a photograph or a drawing of the object, as different information is obtained from observing different sections.

5. The sample should be assigned a unique laboratory number together with sufficient documentation to enable its identity to be preserved.
6. The object should be photographed or drawn before the sample is taken. This is especially important if the dimensions of the object are fundamentally altered by the material removed.

The range of features that may be observed in prepared metallographic sections is variable and depends upon the type of specimen examined and how it is prepared. Details not apparent in the freshly polished state or even after using one etchant may become visible only after another reagent has been employed (which often requires an intermediary return to the grinding and polishing wheels). The following are some of the major microstructure features that can be examined:

1. The range, size, and shape of grains present. Their size can be compared with an eyepiece marked with grain sizes for comparison or with American Society for Testing Materials (ASTM) standard grain size numbers. This sort of data informs us about the fabrication of the artifact (e.g., how intensively the object was hammered before annealing).
2. The presence of different phases, which can be observed either in the corrosion crust or in the metal. This can give us an indication of the ores used to smelt the original metal, the amount of alloying agents added to the base metal, and even how fast the molten metal was cooled (e.g., in an insulated mold or quenched in water).
3. Gross heterogeneity or differences between various areas of the sample. This is important for determining native versus smelted copper, the level of sophistication with which early metalworkers cast metal artifacts, and areas of intensive surface hardening (e.g., working edges of tools).
4. The distribution of inclusions, slag particles, or porosity in the artifacts, which can tell us about the metal refining and casting processes (e.g., in air or under reducing conditions) and sometimes about the direction of hammering due to porosity/inclusion alignment.
5. The presence of any surface coating or gilding. Careful examination at high magnification is necessary to establish the presence of surface treatments that may have corroded or eroded away from macroscopic view.
6. The distribution of any corrosion products present and the existence within corrosion layers of pseudomorphic remnants of grain structure (i.e., grain shapes preserved as ‘ghosts’ in the corrosion) or other microstructural features (e.g., layering).
7. The presence of twin lines (or “annealing twins”) within the grains and whether these twins are straight, curved, or bent. In metals such as copper, silver, and gold alloys, these twins result from the repetitive hammering and annealing of artifacts, thus providing indications of manufacturing techniques.
8. The presence of strain lines (or “slip lines”) within the grains. These features are common in copper and copper alloys and result from excessive hammering without a following annealing step.

9. Whether dendrites (a structure which is common in cast alloys and which may look like an intersecting snowflake pattern) show indications of coring, and the approximate spacing, in microns, of the dendritic arms (if these are clearly visible). These data inform us about the speed at which the cast alloys were cooled.
10. The presence of intercrystalline or transcrystalline cracking in the polished section, which tells us about the mechanical properties of the alloy and the manufacturing techniques used to make the artifact (e.g., high-tin bronzes will crack under excessive hammering without annealing).

Metallographic studies should be integrated as far as possible with contextual data, provenance, chemical composition, and technology of manufacture to extract the maximum amount of information from the removal of a single, small sample from an artifact.

## Phase Diagrams

One of the most useful aids to the study of ancient metals is the equilibrium diagram, also called the phase diagram. Since many alloys are mixtures of two or three different components, phase diagrams are used to plot temperature against composition and to map out the different phases which occur at varying compositions or temperatures in the system concerned. Alloys do not have a particular melting point; they soften and pass through a pasty stage between temperature zones shown on the phase diagram as solidus and liquidus curves. The solidus is the line in the phase diagram that separates the pasty stage of the alloy (usually a mixture of solid and liquid—think of “slush” as opposed to water or ice), from the completely solid alloy (found in temperatures below the solidus line). The liquidus is the line on a phase diagram that shows the temperature at which the alloy begins to cool (i.e., solidify) from the melt. The boundary region between these lines can be narrow or broad. In some alloys of importance in antiquity, such as copper–tin or gold–copper–silver, there is considerable separation between liquidus and solidus curves. This separation exacerbates the difficulties of attaining equilibrium cooling conditions from the melt (i.e., achieving a homogeneous metal alloy), thereby enhancing the segregation effects that can be observed in these alloys. Metastable phases (or regions of compositional variation) may remain within the alloy for thousands of years.

A simple example of a phase diagram is that of the silver–copper system as shown in Fig. 4.1. Copper and silver are not very soluble in each other and form a phase equilibrium where there is a small amount of silver dissolved in copper at one end of the diagram (the alpha phase), and another phase of a small amount of copper dissolved in silver at the other end (the beta phase). Much of the phase diagram is taken up with a two-phase field called the eutectic, which is a mixture of the alpha and beta phases. This results in a whole series of different alloy types in the silver–copper alloys (Scott 2011). Copper and lead, in contrast, are mutually insoluble at room temperature. They will mix together in a melt but rarely will they stay together in a homogenous solution (similar to mixing vinegar with oil to produce a temporary

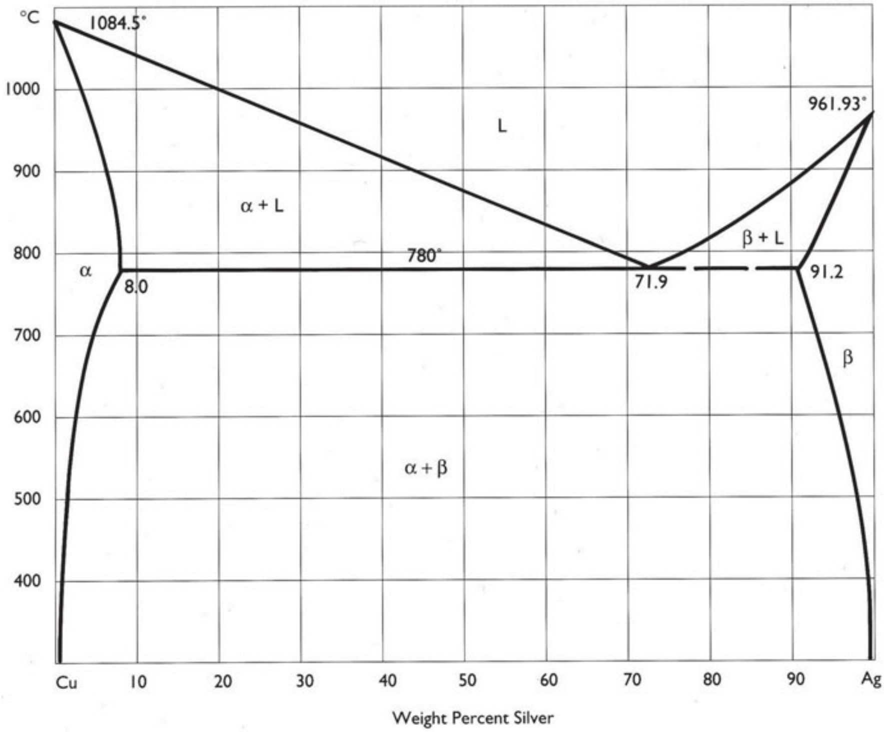

**Fig. 4.1** The silver–copper equilibrium diagram (after Scott 2011). The solidus line is the *straight line* running horizontally across the diagram at 780 °C. The liquidus lines are the *two upper sloping lines* which intersect at 71.9 % silver. The $\alpha + \beta$ phase *below the solidus line* is solid. The *L* phase *above the liquidus lines* is liquid. The $\alpha + L$ and $\beta + L$ phases *between these lines* is a pasty or "slushy" intermediary phase

vinaigrette that must be shaken constantly to remain in solution). For example, if a copper–lead alloy is left to cool too slowly, the resulting metal will be weakened by large globules of lead that separate out of solution. Copper–silver alloys do not have this problem.

To the left of this diagram is pure or nearly pure copper ("α"; melting point of pure copper: 1084.5 °C) and to the right, pure or nearly pure silver ("β"; melting point of pure silver: 961.93 °C). When copper and silver are mixed together, the alloy system creates a low melting-point eutectic ("α + β") at temperatures below 780 °C, i.e., far below the melting point of the two pure constituents (thereby explaining one of the main benefits of alloying metals). This eutectic will have a composition of roughly 71.9 wt% Ag and 28.1 wt% Cu at 780 °C, which is the "eutectic point" at which liquid metal will cool instantly to the solid phase without an intermediary pasty or "slushy" stage. Under ideal conditions, the system will always move toward the eutectic point.

For example, let us say that you have a molten alloy with 30 wt% silver and 70 wt% copper. As the melt cools, metal will begin to solidify (into the pasty "α + L" phase) at the liquidus line (around 950 °C, in this case). What crystallize first, however,

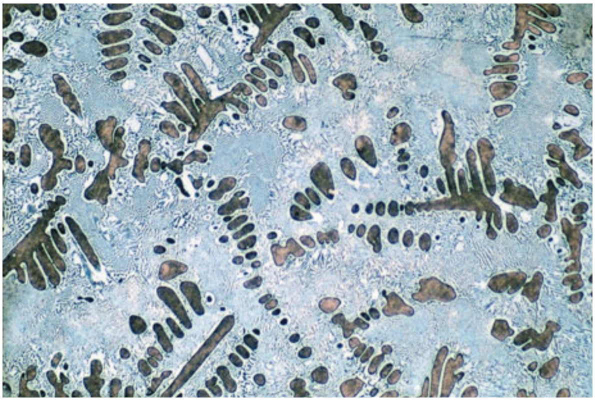

**Fig. 4.2** Photomicrograph of a cast laboratory copper–silver ingot with a composition close to the eutectic point. Slow movement toward equilibrium in this binary system (i.e., slow cooling times) resulted in copper-rich dendrites (*brown*) surrounded by the eutectic mixture (*blue*), which consists of the α and β phases as a fine interlaced mixture. Etched in potassium dichromate, × 260

are dendrites containing 70 wt% Cu and 30 wt% Ag. This solidification obviously removes more copper from the melt than silver, thereby changing the composition of the remaining melt to something more like 32 wt% silver and 68 wt% copper. Changing the composition of the melt also changes its cooling point on the liquidus line—in this case, shifting it to the right, thereby lowering the melting temperature. As more metal crystallizes out of solution, the molten alloy will 'slide' down the liquidus line towards the eutectic point. Once the alloy goes below 780 °C, the entire melt is now solid. What you see in the microstructure, then, are dendrites of varying compositions (in this hypothetical case, with Ag:Cu ratios ranging from 3:7 to 7:3) surrounded by a matrix of eutectic (i.e., metal with a composition of 71.9 wt% Ag and 28.1 wt% Cu). This sort of microstructure can be seen in Fig. 4.2.

In contrast to the example shown in Fig. 4.2, alloys which are high in silver, such as a typical sterling composition silver (about 8 % copper and 92 % silver), will form only small areas of the eutectic mixture with large dendrites of silver-rich β phase. The same kind of structure is found at the copper-rich end of the phase diagram, with copper-rich α dendrites surrounded by a small matrix of the $\alpha + \beta$ eutectic. However, in ancient silver alloys (which may or may not be remelted for casting), this kind of ideal structure may be overshadowed by metastable copper within the silver-rich grains that gradually segregates out of solution over the millennia. Such metastable copper can appear due to quenching of silver alloys during working (thereby freezing the metal into metastable alloys) or due to dendritic segregation, in which the initial dendrites are just flattened out by hammering into thin stringers and never actually disappear from the microstructure.

In most of these equilibrium diagrams, we talk about a phase. A phase is usually a component of variable composition which occurs within set boundaries of variation in terms of composition and temperature. For example, the alpha phase in the copper–tin system may contain as much as 14 % of tin and still be a homogeneous single phase. More commonly, if the alloy is not thoroughly annealed, the amount of tin which enters into solid solution with copper in the alpha phase is variable and usually between 5 and 8 wt% Sn. The remainder forms what is called a "eutectoid phase," which in the bronze system arises from the decomposition of a higher temperature

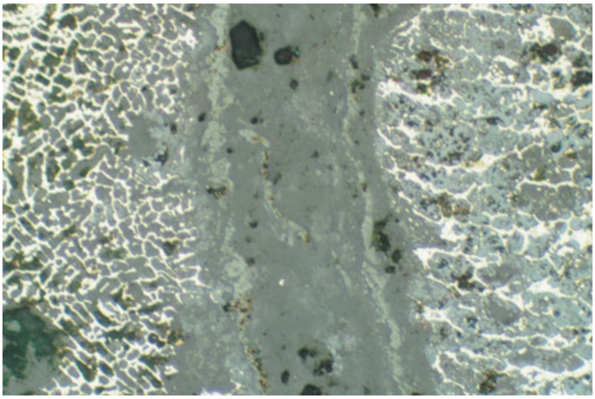

**Fig. 4.3** Photomicrograph of a section through a face stud from the site of La Compaia, Los Rios Province, Ecuador, dated to about the tenth century AD. On the *left-hand side* is the as-cast dendritic structure of the spherical ball of silver–copper alloy used for the head. To the *right* is the worked and annealed structure of the shaft of the face stud, which has been joined by depressing the worked shaft into the heated ball of the head. Corrosion (*gray, in middle*) has occurred extensively at the join area. Unetched, × 220

**Fig. 4.4** Linear Elamite silver bucket dated to about 2000 BC. The inscriptions on this very rare artifact cannot be read, which has led scholars to suggest that the bucket is a forgery. (Photograph courtesy of Pieter Meyers, Los Angeles County Museum of Art)

phase (which is why it is called a eutectoid rather than a eutectic). Dendritic growth, which is a form of compositional segregation during cooling, tends to dominate the world of ancient castings. Once formed, the segregation caused by dendritic growth is hard to eliminate, even by extensive working and annealing to shape (see Fig. 4.3).

Many silver objects were made with deliberate but small additions of copper, these alloys frequently having 1–6 % of added copper. If the copper additions are sufficient, some of the copper is kept in metastable solid solution with the silver during working and annealing. The result is a slow precipitation of the copper over long periods of time, resulting in the grain boundaries of the silver becoming displaced and forming small meanders in the solid. This is due to the discontinuous precipitation of copper at the grain boundaries, and is good evidence of age. A nice example of this is shown in Fig. 4.4, which is a Linear Elamite-inscribed silver bucket originally from southern Iran now in the collections of the Los Angeles County Museum of Art. This bucket

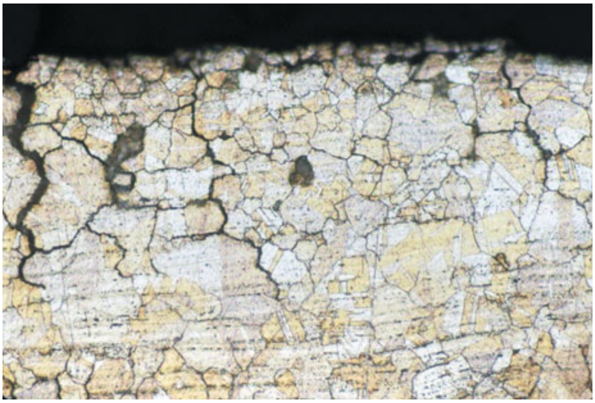

**Fig. 4.5** Microstructure of the Linear Elamite silver bucket, showing cracking through some of the grains due to corrosion and weathering. Occasional twinned crystals suggest working and annealing. More importantly, discontinuous precipitation of copper at grain boundaries (visible as *thin black lines* strung out *horizontally across the sample*) results in the meandering boundaries seen here and provides nearly incontrovertible evidence of authenticity. Etched in acidified potassium dichromate, × 270

of uncertain provenance was dismissed by many art historians as a fake, given that there is practically no corrosion and Linear Elamite inscriptions are rare and not well understood.

However, metallographic analysis of a section from this bucket demonstrates the classic discontinuous microstructure shown in Fig. 4.5. There can be no doubt whatsoever that this bucket is authentic.

## Case Studies

### *Melting and Casting*

Metallic materials can be deformed by hammering ("plastic deformation") or they can be melted and cast into shape. The temperatures attainable with an enclosed charcoal fire or a wood fire with forced draught are generally high enough to melt most of the metals and alloys used in antiquity, with the exception of wrought iron and platinum (neither of which were used from the molten state). On a microscopic level, casting of most metals produces a segregation (or "compositional separation") of different alloy components of the melt as they freeze or solidify out of the cast state. Dendritic segregation, in which small fernlike growths solidify out of the melt and grow toward each other until the liquid metal is consumed (i.e., the metal is now entirely solid), is the most common form of compositional separation as a result of casting.

A fine example of dendritic segregation can be seen in a tin–bronze dagger handle from Luristan, Western Iran, containing about 17 wt% tin (Fig. 4.6). Due to differential freezing temperatures among alloys of varying compositions, the primary alloy

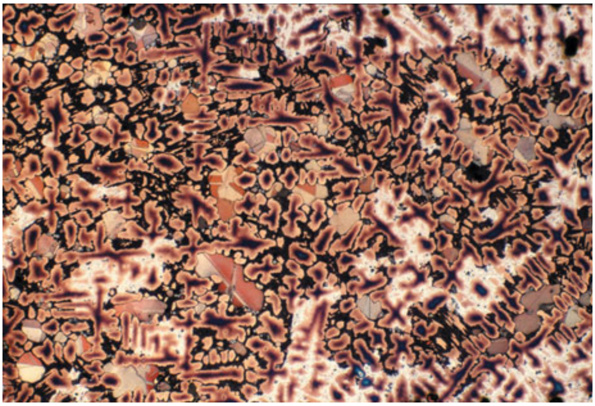

**Fig. 4.6** Photomicrograph of a tin–bronze dagger handle from Luristan, Western Iran, dated to ca. 1500 BC, which shows a fine cast structure of the handle with about 17 % of tin. The metal is heavily cored between low-tin (*redder*) and high-tin (*whiter*) phases and contains twinned crystals of redeposited copper as a result of corrosion. Color etched in lead thiosulfate to reveal the segregation in the cored alpha phase, × 280

tends to solidify in these snowflake-like patterns, pushing extra components of the metal to the background areas around the resulting dendrites (white and black phases in Fig. 4.6). Among the dendrites and background matrix, twinned crystals of redeposited copper can be seen (e.g., bottom left of Fig. 4.6). Redeposited copper often appears in ancient copper and bronze alloys because of the breakdown of copper due to environmental factors in deposition. The loss of the tin-rich phase may be another reason why copper redeposition occurs in this bronze.

Etching the polished surface of a metallographic section is necessary to look for evidence of casting structures, although in some cases it is too destructive to the patina to use an etch if the corrosion crusts must be examined. It should be mentioned that in addition to dendritic segregation, so-called “inverse segregation” may also occur in ancient metals. This phenomenon, in which the lower melting point constituent, such as tin or arsenic is preferentially forced to the outside surface of the casting, is particularly common in copper alloys. For example, “tin sweat” occurs in tin bronzes when tin-rich liquid, which is the last phase to solidify, moves through copper-rich solidified dendrites to form a whiter surface enriched in tin at the expense of the bulk alloy.

## *Hammering and Annealing*

One of the most common applications of metallography in archaeology is to determine the manufacturing techniques used to make metal objects in the past. As discussed in the chapter by Notis in this volume, the plastic deformation of metals through hammering and annealing (or simply hot working/forging) causes a number of changes to the internal structure of the metals. These microstructural features,

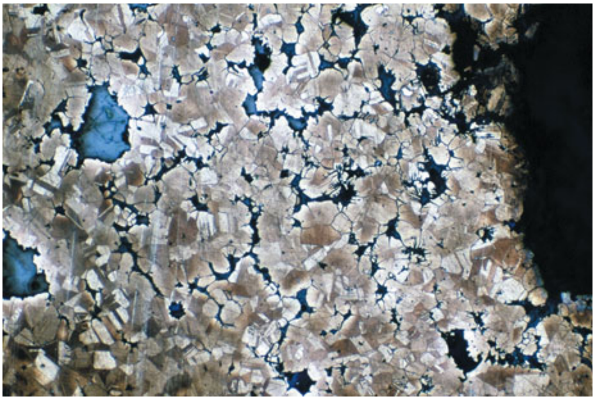

**Fig. 4.7** Section through a tin–bronze flanged axe from Ireland dated to 1700 BC and containing roughly 8 wt% tin. The recrystallized grains show annealing twins, while crystals of redeposited copper appear blue as a result of corrosion. Strain lines, just visible *on the edges* of the image, occur as a result of the slip of crystal planes over one another in the bronze. Color etched in acidified thiosulfate, × 320

such as dendrites, grain boundaries, annealing twins, slip/strain lines, and so forth, can be observed and documented using only metallographic methods.

An example of a copper alloy that has been cast, cold worked, and annealed is shown in Fig. 4.7. The section was taken from an Early Bronze Age flanged axe dated to about 1700 BC from County Clare, Ireland. Although the flanged axe was cast in an open mold and might be expected to show a dendritic structure, these Bronze Age axes were often finished by hammering and annealing of the cast form to shape the final product. When an annealed object with twinned grains is cold worked, the twin lines become deformed and will no longer appear straight. This is indicative that the final stage of fabrication was cold working. Additional features that indicate a final cold-working step after annealing include strain lines, which may be visible in the metal after etching.

## *Quenching of Bronze Alloys*

For low-tin bronzes, rapid cooling (such as quenching the hot metal in water) affects the extent of dendritic growth, but the overall effects upon the microstructure and mechanical properties of these bronzes would be slight. However, if the tin content is raised to around 20 %, then some of the higher temperature phases present in the copper–tin phase diagram (see figures later in the chapter) can be retained by quenching, producing an alloy with very different working properties than the cast equivalent. If such high-tin bronzes are used to produce mirrors or decorative vessels, then the mechanical differences are not so important for the functional use of the object. These differences become significant if the object is finished by turning on a lathe or if it has to be cut and decorated after casting. Then the advantages of quenching these bronzes become apparent because the alloy is considerably less brittle in the beta-phase region and can be turned on a lathe or hot worked, which the high-tin alloys can usually never be. The beta bronzes allow metalworkers to produce slivery-colored alloys with high-tin content, without the brittleness associated with bronzes of the same composition which have been allowed to cool slowly, resulting in a microstructure of alpha + (alpha + delta). Such alloys have no ductility whatsoever, and if dropped on a hard surface, they will shatter into pieces, breaking along the delta phase. Quenching suppresses this microstructure completely.

Two versions of the copper-rich end of the copper–tin phase diagram are shown in Fig. 4.8. The left-hand view shows what the lower tin-content alloy phases would be at full equilibrium under normal casting conditions, while the right-hand view shows the typical limit of the alpha solid solution under different casting conditions. If the bronze is cooled more quickly, as in chill casting, there is less of the alpha phase and more of the alpha + delta eutectoid, while if it is cooled more slowly, more of the tin is taken into solid solution with the copper, and the field of the alpha phase expands to incorporate more tin and less eutectoid.

An example of the microstructural effects of quenching is shown in Fig. 4.9, part of a high-tin bronze bowl (22.7 wt% Sn and 76.2 wt% Cu) from the site of Ban Don Ta Phet, Thailand, dated to about 100 AD. Examination of the etched section shows the presence of some alpha-phase copper-rich grains, which occur in areas with specific orientation as well as in a random scatter, showing that the metalsmiths were aiming for a specific composition which had a combination of mechanical toughness, high hardness, and a lustrous surface. The technological process was therefore very sophisticated and was dependent on being able to cast an initial alloy with very closely defined composition parameters. If the tin content was too low, around 18 % the beta phase would not form, and if the tin content was too high, the mechanical properties of the alloy might not be so amenable to turning on a lathe or hot working followed by quenching. The fact that the microstructure consists of a mixture of twinned alpha grains with an acicular infill of beta needles argues for the mechanical benefits of the intimate mixture of the two phases in improving workability from the quenched state. The alpha grains are softer and can act as stress-relieving areas or as softer components of the structure which allow for the manipulation of the alloy by hot working more readily or by acting as areas of softer metal for turning on a lathe to finish part of the surface decoration. The relationship between technological process and alloy composition in this case is a very precise and well-controlled one. Analysis of some of the background phases even allows us to reconstruct the temperature of the bowl when it was quenched. This give us important information about what the ancient metalworker was trying to accomplish, as quenching high-tin bronzes at different temperatures will result in metals with very different properties. The sophisticated metallurgy of these bowls would be impossible to unravel without metallographic investigation.

In some metals, such as tin bronze, gold alloys, and iron alloys, there may be advantages to quenching the alloy from a high temperature. These benefits include

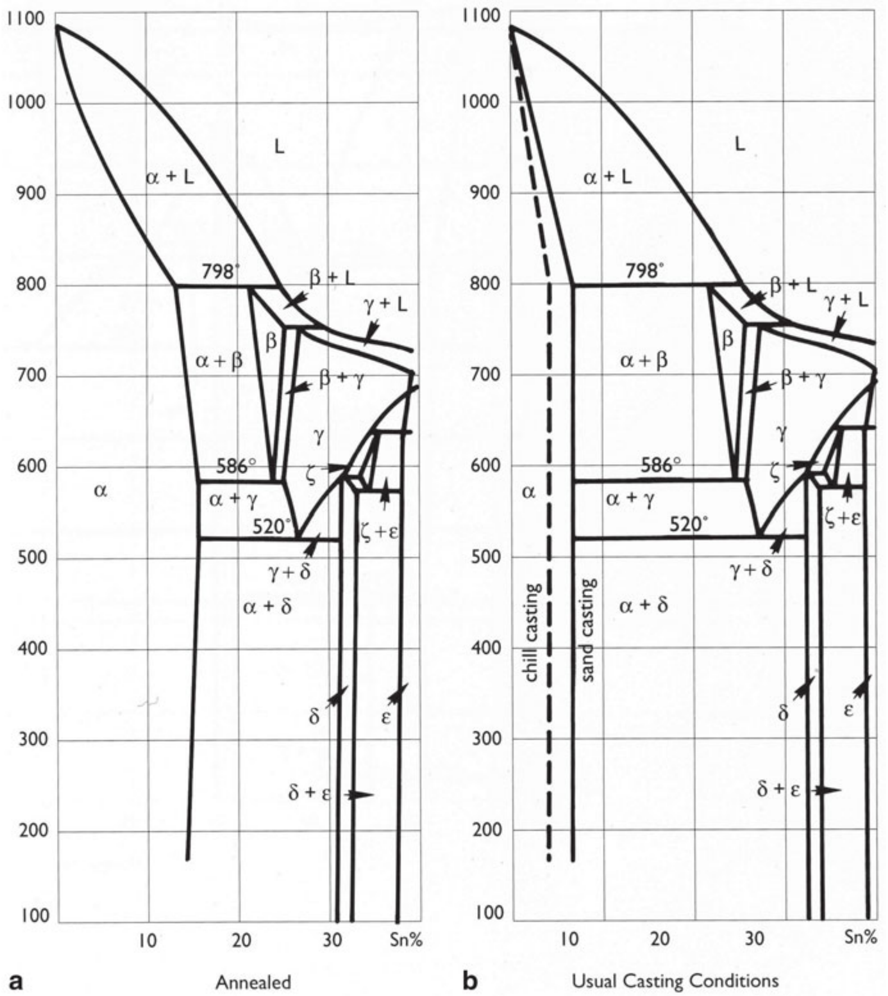

**Fig. 4.8** Partial versions of the copper–tin phase diagrams showing **a** the full equilibrium view of the extent of alpha solid solution and **b** the actual extent of solid solution depending on casting conditions. (Redrawn from Scott 2011)

either retaining certain phases which are only present at high temperatures, or preventing lower-temperature phases from forming, which might lead to embrittlement. Thus, many gold alloys are quenched to prevent ordering reactions from occurring. Ordering reactions result in the formation of compounds with fixed composition which behave more like minerals than metals. They have very limited ductility and are responsible for cracking and hardening of some alloys over time. These ordering reactions produce phases of fixed composition such as AuCu, which have rather limited ability to be deformed by hammering or working, and which can result in

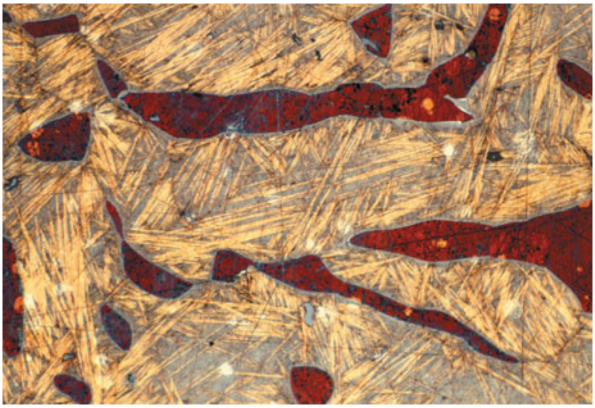

**Fig. 4.9** Section of a high-tin bronze bowl from the site of Ban Don Ta Phet dated to about 100 AD with a composition of 22.7 wt% tin and 76.2 wt% copper. The beta-phase needles appear *straw colored* and the copper-rich alpha-phase grains appear *red*. Twins in the alpha phase can just be seen, showing that the bowl has been hot worked from the beta region. Color etched in Klemm's number 2 reagent, × 280

cracking of the gold alloy on working. Hence, in this case, quenching makes the metal softer and less brittle, while many steels are quenched to form martensite (a high-temperature phase), which makes them harder and brittle; therefore, the technological processes associated with quenching have to be tailored for the alloy concerned.

## Surface Treatments

Metallic artifacts are often not what they pretend to be, but are treated on the surface to look like a different metal (e.g., gold or silver plating). Figures 4.10 and 4.11 show the microstructure of a bronze belt buckle from the Han Dynasty of China, the surface of which was dipped in metallic tin (known appropriately as "tinning"). The common metallic phase which results from many of these tinned surfaces is the so called $\eta$ phase, which has a composition of $Cu_6Sn_5$, rather than metallic tin *per se*.

Many different kinds of surface treatments and coatings have been developed in different cultures for different purposes. Figure 4.12 shows a section of a Roman coin of Augustus, plated with a silver–copper alloy, which is then treated to create a silver-enriched layer on the surface. The plating of the silver–copper alloy could be carried out either by a dipping process or by the application of silver–copper filings to the surface followed by heating ("fusing") in place.

Another example is a Parthian silver rhyton in the collections of the J. Paul Getty Museum that has been gilded, although this time the base metal is silver. The lion rhyton is shown in Fig. 4.13: a masterpiece of ancient silver working.

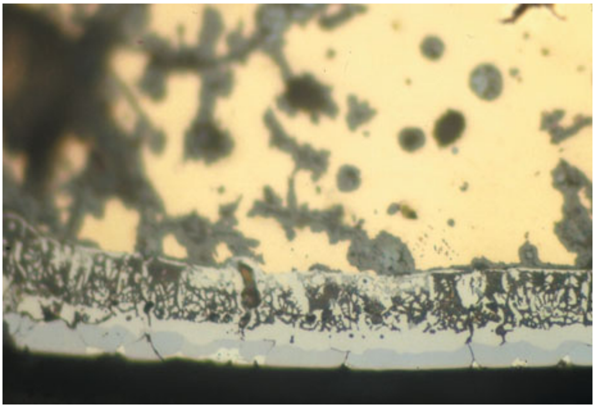

**Fig. 4.10** Section through a Han period Chinese belt buckle showing that the surface has been tinned. The very *white* phase *near the outer surface* is metallic tin, followed by the *grayish* eta (η) phase, the *whitish* epsilon (ε) phase, and the (α + δ) eutectoid phase before the low-tin bronze of the cast belt buckle is reached. Unetched, × 460

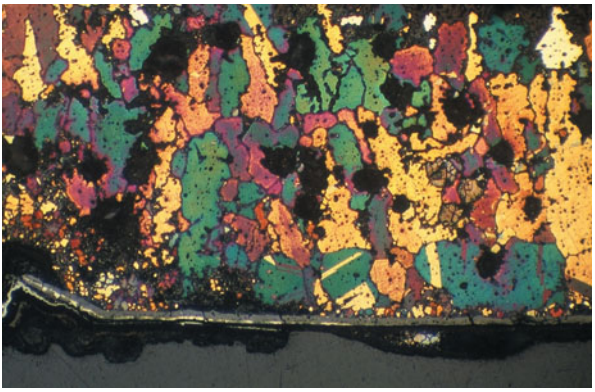

**Fig. 4.11** Photomicrograph of a tinned Han belt buckle showing the essentially cast matrix of the buckle. Note the presence of a few annealing twins toward the outer, tinned surface, showing that some working and annealing has been employed to shape the surface before the application of the tin. Color etched in lead thiosulfate etchant, × 150

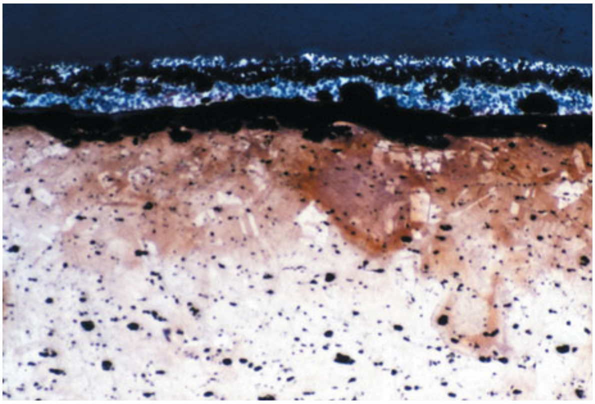

**Fig. 4.12** Etched view of a Roman bronze coin of Augustus, showing silver fusion-plated over leaded copper. The silver coating is close to a eutectic mix to prevent melting the coin when applied. Etched in alcoholic ferric chloride, × 280

A section was taken from a small break under the body of the rhyton and the extent of the gilding investigated. The gold foil is quite thick and has been applied by diffusion bonding of the foil to the underlying silver, as seen in Fig. 4.14. Diffusion

**Fig. 4.13** Lion rhyton in the collections of the J. Paul Getty Museum, Parthian first century BC. The lion is also decorated with garnets. (Photograph by David A. Scott. Also by courtesy of the J. Paul Getty Museum at the Villa, Malibu, California)

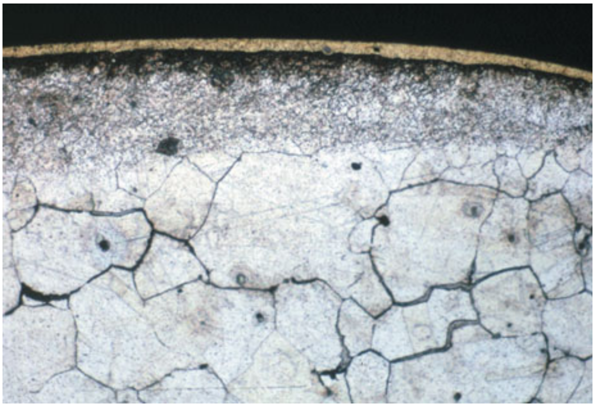

**Fig. 4.14** Gilded silver rhyton in the collections of the J. Paul Getty Museum, showing thick gold foil and the characteristic cracking and discontinuous precipitation of the silver grains. Etched in acidified potassium dichromate, × 320

bonding is the application of a metal coating to a substrate, with careful heating to bond the two metals together. The two different metals will diffuse into each other at different rates, but produce a bond which is metallurgical and not mechanical, as the hammering of a gold foil over silver would be. The metallurgical bonding achieved by diffusion bonding is much more permanent than those bonds achieved by mechanical methods because in the mechanical attachment there are no permanent metallic bonds created by the union of the two components.

In pre-Columbian South America, the preferred surface treatment technology was “depletion gilding”, in which gold–copper–silver alloys (“tumbaga”) are pickled in plant or other corrosive substances to leach out most of the copper. Silver is not removed in this process as the plant juices cannot complex with the silver. This process leaves a gold-enriched surface on an artifact that may only contain 15–20 wt% of gold, but which appears to be solid gold on the surface. An example of this technique from Panama is shown in Fig. 4.15, where the thin, spongy, gold-enriched surface was burnished to create a flat, golden surface (with only about 25 wt% gold content) over the artifact.

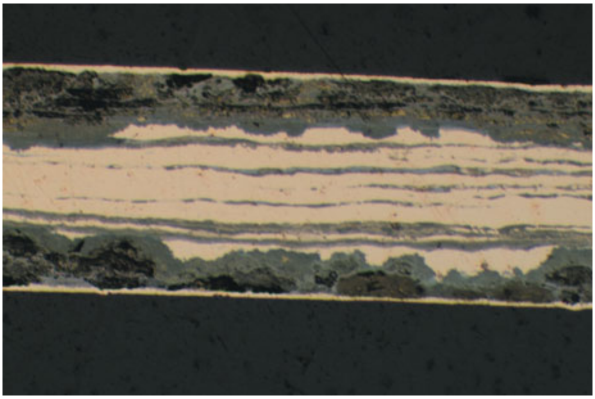

**Fig. 4.15** Photomicrograph of a fragment of a sheet gold ornament. It is a tiny fragment (so the nature of the original artifact is not known) from excavations at the site of Sitio Drago, Panama, dated to about 1100 AD. This golden-colored artifact was shown through metallography to be a depletion-gilded gold–silver–copper alloy with heavy corrosion under the gilded surfaces. The striated interior structure of the tumbaga fragment was caused by heavily working the metal into a thin sheet, leading to some dendritic segregation of the different components of this ternary alloy, which are strung out along the length of the sheet as a result of the working and annealing process. Subsequent corrosion beneath the depletion-gilded surfaces has exaggerated the compositional differences. Unetched, × 180

In Peru, different techniques of surface treatment were employed, using mineral pastes capable of removing both copper and silver from the surface of the artifacts. Metallographic examination of these surface-treated alloys is essential for the proper identification of the materials used and interpretation of the technological processes used in their manufacture.

## Corrosion

Examination of corroded sections is often an essential component of authenticity studies of antiquities, and metallographic studies are crucial to this process. In copper-base alloys, the presence of cuprite ($Cu_2O$) within the corrosion crust and the degree to which cuprite has penetrated into the metal are both indicators of authenticity. For example, a series of bronze plaques that were supposedly found in the Fayum region of Egypt have appeared in a number of museums (see Fig. 4.16). If authentic, these plaques are important because they are inscribed with some of the earliest Greek writing known to scholars.

Metallographic examination of this plaque (Fig. 4.17) reveals a clear cuprite layer between the copper-base metal and the malachite-base corrosion (i.e., patina). This sequence of layers as seen in the photomicrograph is generally a good indication of authenticity.

**Fig. 4.16** Greek plaque reputedly found in the Fayum region of Egypt and dated to the ninth century BC based upon the inscription. The plaques, of which five probably existed, preserve one of the earliest versions of the Greek language. (Photograph courtesy of Professor Bruce Zuckerman, University of Southern California, Department of Religion)

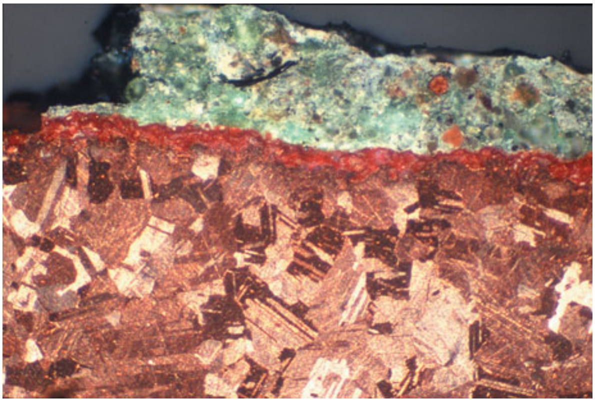

**Fig. 4.17** Cross section of the Greek copper plaque from Fig. 4.16, showing the presence of a good red cuprite layer overlaying twinned and recrystallized grains of worked copper. The red cuprite layer is overlain by a complex, principally malachite corrosion layer incorporating mineralized wood fragments, dirt and other mineral grains, and charcoal fragments. Etched in alcoholic ferric chloride, × 340

## Iron and Steel

The first iron materials used by man were meteoritic, which had fallen from the skies and could be picked up as small pieces or laboriously broken off from larger masses of iron. The problem with the use of meteoritic iron was that it contained a substantial

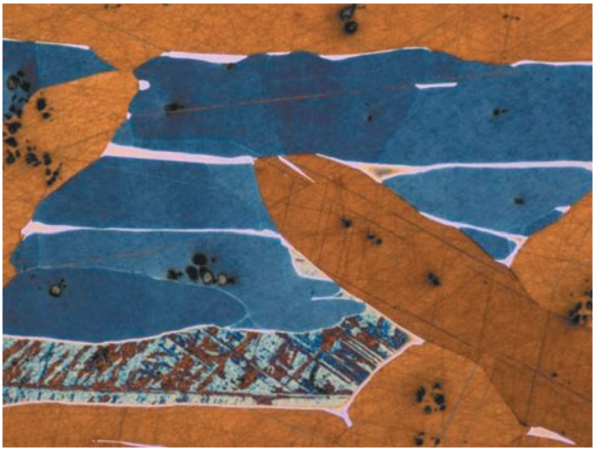

**Fig. 4.18** Polished and etched photomicrograph of a meteorite from the Gibeon, Great Nana Land, Namibia, showing part of the complex structure of this iron–nickel alloy. The phase called taenite here etches a *yellow* color, while kamacite is *blue*. A plessite field can be seen in the *crosshatched pattern toward the bottom* of the picture. Color etched in Klemm's number 1 reagent, × 230

amount of nickel and often carbon as well, resulting in an incredibly hard material which could not be molten and could only be shaped by hammering with considerable difficulty. Figure 4.18 shows a color-etched interference-tint photomicrograph of a meteorite from the region of the Gibeon, Great Nana Land, Namibia, where large falls of small pieces of meteoritic iron resulted in their use for jewelry and personal adornment at an early date. The metallographic image shows part of the structure of the meteorite with iron-rich phases in pale yellow and the iron–nickel alloy in dark blue, with a fine precipitate under the blue laths in the picture being a precipitate of one iron–nickel phase in another. This is the unworked microstructure of the different phases in the meteoritic iron.

Iron and low-carbon steel alloys, particularly in the Western tradition, were usually produced from bloomery iron, which means that they have never been molten or cast (instead exiting the furnace as a spongy, slaggy mass that must be refined through forging). Bloomery iron artifacts are often made from small pieces of iron/low-carbon steel welded together to create the finished object. As a result, weld lines, enrichment zones, phosphoric iron, and low-carbon steel areas may all be present in the same object. A typical wrought-iron/low-carbon steel, albeit from a twentieth-century sculpture ("Night Presence II" in San Diego), is shown in Fig. 4.19. Examination of the section reveals a "Widmanstätten" structure. This structure arises from the decomposition of a solid solution phase at a higher temperature into two distinct phases at lower temperatures. So here, the higher-temperature austenite solid solution decomposes on cooling into alpha grains of iron and an infill of the eutectoid phase of alpha iron (ferrite) and cementite, known as pearlite, because iron of the eutectoid composition fractures with a pearly luster if the carbon content is about 0.8 %.

The carbon content of early iron artifacts may be variable too, most being made of low-carbon steel with less than 0.8 % carbon (often much less than that). Steels may have up to 1.2 % carbon, the 0.8 % level being the eutectoid, known as pearlite, which is a fine mixture of ferrite and cementite. Ferrite is essentially pure iron, while cementite is a compound of fixed composition ($Fe_3C$). Phases of fixed chemical

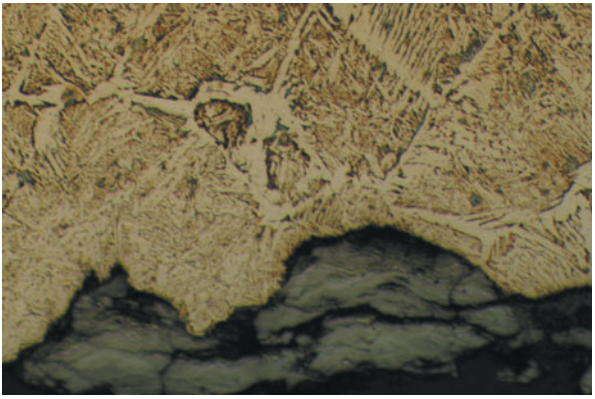

**Fig. 4.19** Section of the sculpture “Night Presence II” in San Diego, showing corrosion penetration and the jagged structure of the low-carbon steel used to fabricate it. The use of this heterogeneous low-carbon steel has resulted in extensive corrosion failure. Etched in 2 % nital, × 450

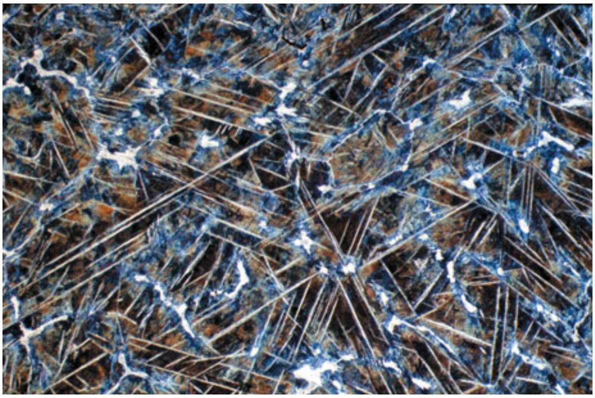

**Fig. 4.20** A hypereutectoid steel Wootz cake from the Deccan region of India showing a very clean iron microstructure with no slag. The carbon content is about 1 % and the microstructure has a mixture of cementite needles and finely-spaced pearlite, here etched a *dark brown* in Klemm’s number 1 reagent, × 300

compositions such as cementite are usually hard but lack ductility. The great variation in the microstructure of steels, depending upon heat treatment and alloying components, causes the microstructure of steels to be especially revealing of technological processes. An example of a high-carbon steel is shown in Fig. 4.20, from the Deccan region of India. This Wootz steel ingot was made in a crucible during the eighteenth century AD and is effectively a cast product. The long white needles in the photomicrograph are of cementite and the background is of pearlite.

Quenching wrought iron has little effect upon the working properties of the metal. However, with a more significant carbon content (0.3–0.7 %), it was soon appreciated that quenching could produce a much harder alloy. By quenching a forged iron blade, a much stronger edge could be achieved.

Cast iron was manufactured in China long before the Western world was able to produce it. Chinese metalsmiths excelled in the production of white cast iron, in which the excess carbon is taken up as cementite rather than graphite. An example of a Chinese cast hoe is shown in Fig. 4.21. The carbon content of this cast iron is about 3.5 %, and it is a white cast iron. The principal problem with Chinese cast iron

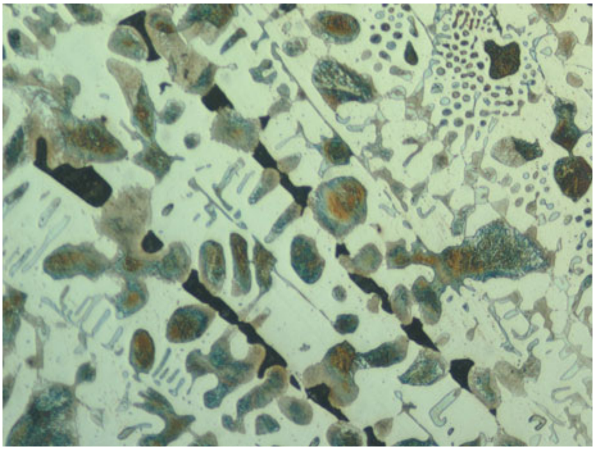

**Fig. 4.21** White cast-iron hoe from the Gansu region of China, Warring States Period. The structure shows primary laths of cementite (the *long white phase*) with proeutectoid pearlite (the *straw-etching phase*) and patches of the eutectic ledeburite (the *structure with a series of fine holes*). Etched in 2 % nital, × 340

was that, unlike the wrought iron and low-carbon steel used in the West, the carbon content of cast iron has to be reduced in order to make useful tools and weapons.

The process of decarburization, that is, the deliberate loss of carbon as a result of heating in air, can be used to reduce the carbon content of cast irons or high carbon steel, to make a softer product, especially since cast irons are very brittle. Decarburization was often used to make iron artifacts of lower carbon content out of cast iron. When high-carbon steels or cast irons are heated to high temperature and a blast of air applied to the melt, some of the carbon content is oxidized, the brittleness associated with the higher-carbon cast iron is lost, and the whole mass begins to solidify as the carbon is reduced. This is the process of decarburization. The Han sword section shown in Fig. 4.22 is unusual in that it appears to have been hammered from bloomery iron. Extensive segregation bands (in copper and nickel) have resulted from the making of this sword, probably as a result of a series of folded laminations from a hammered-out bloom of iron. These laminations are also typical of low-carbon and phosphoric iron from the West, but here the Chinese example is very much cleaner with practically no slag inclusions and has a carbon content close to that of the eutectoid composition at 0.8 % carbon, which is a high-quality carbon steel product. As the iron in the West was produced in the bloomery process, it was never fully molten and the mass of material that was worked up by the metalsmith included unreacted ore, glassy slag waste, and heterogeneous iron lumps. With forging, the impurities were mostly removed with some slag occurring as stringers within the worked bloom. Phosphoric iron results from the use of iron ores containing phosphorus, so that some of the phosphorus is present in the smelted iron bloom and causes a number of changes in properties of the iron, some of which are beneficial. For example, phosphoric iron may be harder and take a better edge than pure wrought iron. Since most of the iron of the ancient world was produced in the bloomery process, the iron needed to be heated to red heat and hammered out to consolidate it, removing in the process most of the slag, but some iron artifacts retain a lot of slag stringers within the finished object. Slag, usually the glassy mineral

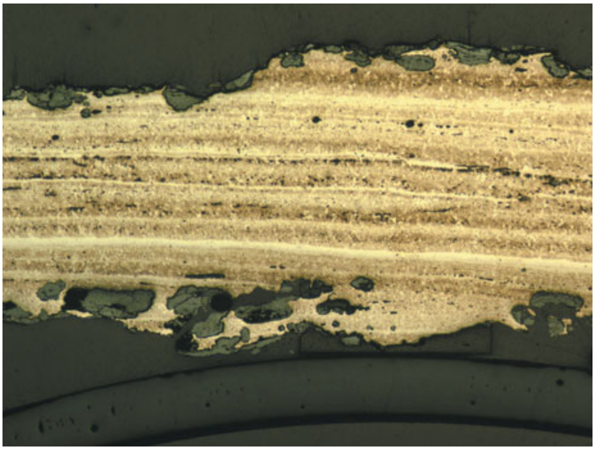

**Fig. 4.22** Microstructure of a Han Dynasty sword blade from Gansu Province, China, showing a finely laminated structure as a result of folding and working of the hypereutectoid steel used to make this blade. The *white bands* are enrichment zones (usually at weld lines) of copper or nickel. The number of parallel laminations probably results from the folding of the iron over and over again to create this type of microstructure, often seen in low-carbon steel blades in the West. Etched in 2 % nital, × 160

fayalite in ferrous materials, cannot recrystallize on working of the iron and becomes elongated and flattened during hammering into stringers.

## Summary

Metallography is the science of the examination of metallic materials employing optical microscopy or SEM to investigate structure and composition of the polished surfaces of the object. Metallography is an indispensible tool in the study of ancient metals and the by-products of metallurgical processes. It can tell us a great deal about the process of fabrication of ancient metals and alloys, revealing casting, cold working, annealing, heat treatments, alloying, and quenching. Metallography can reveal the nature of surface coatings, gilding, silvering, or other forms of surface treatment. The extent of corrosion, deterioration, or aging of alloys can also be investigated. The future of metallography includes the increasing use of nondestructive techniques to probe inside the structure of metals without the need to remove a sample, as well as new methods of nanoscale analysis which will enhance the interpretation of microstructure of ancient materials. Conventional metallography will continue to be an important part of a comprehensive study of metallic materials from a culture or excavation and it should always be incorporated in comprehensive site reports and publications. The use of digital file sharing will mean that many color images of microstructures can be studied in the years to come, without the current restrictions on the use of color in published books, which has always acted as a hindrance to the full appreciation of the metallography of ancient metals. Continued progress in the study of ancient metals reveals to us the often complex nature of the metallurgical developments which took place in different periods and cultures: metallography has a central role to play in understanding how societies manipulated materials and made choices as to how their technology was going to be developed or utilized. The examination of cross sections of ancient artifacts is especially important in heterogeneous materials, such as early wrought iron and steel, in which metallography can reveal so much concerning the fabrication history of the artifacts and the kind of alloy chosen for use and is important in the study of coated or gilded materials where a bulk analysis will not reveal the nature of the interior of the artifact distinct from the surface zones, which may be of very different composition. Aspects of authenticity in terms of the extent of corrosion, discontinuous precipitation, or type of corrosion are important components of the study of ancient metals, especially bronzes, and in the case of embrittled alloys, such as ancient silver.

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