Etching Solutions

This section deals with etching solutions that can be used for archaeological metals. Further details regarding etchants can be found in the literature referred to in Chap. 3. The listing below is therefore very selective and represents the etchants which have been found useful in the experience of the authors.

As regards the solvents used in etching solutions, water (H_2O) should be distilled water, and ethanol (C_2H_6O) should be anhydrous (99%) or not less than 95% alcohol. All chemicals refer to common commercially available concentrated laboratory grade substances and must be handled with care and in accordance to laboratory safety regulations currently in force in the laboratories concerned. The manufacturers of these chemicals also provide safety data sheets which can be consulted for further information regarding storage, handling and use.

Before etching, ensure that the sample is as scratch-free as possible and that the surface is free of oil, water or ethanol staining, as these will all interfere with the correct etching of the sample. Some samples are liable to be stained on etching due to the presence of different phases, holes or interdendritic porosity. In such cases the sample should be carefully washed in ethanol after etching and dried as thoroughly as possible to prevent excessive staining. Samples can be repolished, cleaned in ethanol and then dried and re-etched. This is often advisable if the finish is less than desired on the final polishing and first etching.

For etching the sample can be held in a pair of tongs, of which there are many different types available. Make sure that there is enough room in the etching tray, often a crystallizing dish, for the sample diameter and the tongs to be immersed into the etching solution. Use gentle agitation if possible while etching to avoid stagnant conditions and uneven etching. Samples after etching can be stored in an efficient desiccator or simply repolished and dried if exceptionally valuable. Samples with etched surfaces will continue to corrode, and in the case of iron artefacts, this can be severe with filiform corrosion of exposed surfaces being a common phenomenon. Sound metallographic principle dictates that all specimens should be examined in the unetched state before proceeding to etching. This is partly because etching may

D. A. Scott, R. Schwab, *Metallography in Archaeology and Art*, Cultural Heritage Science, https://doi.org/10.1007/978-3-030-11265-3

dissolve out any non-metallic inclusions or adversely affect the examination of patina and corrosion which can be essential in authenticity determinations.

Health and Safety

Observe all health and safety regulations pertaining to the country in which you are working.

Many etchants, such as nital, are only partially stable and tend to alter over time in their bottle. Make up small quantities of etchants if just for your own use, as this not only ensures that the etchants are fresh but also saves money on chemical supplies. Many of the preparations described here are poisonous or have to be used in a fume hood, depending on local regulations.

Etchants for Iron, Steel and Cast Iron

Nital 95–99 ml ethanol and 1–5 ml nitric acid. The 2% solution is the most common. Nital is the most useful general etchant for most iron alloys. The strength of the nital solution tends to vary over time, and if no etching appears in a reasonable time frame, the worker can try adding a few drops of nitric acid to the solution to increase acid strength.

Picral 100 ml ethanol and 2–4 g picric acid. The 4% solution (saturated) is the most common. Picral is a very useful etchant for iron and carbon steels. Often used for iron and heat-treated steels, pearlite and martensite. Cementite is stained a light yellow. This can be very useful in distinguishing ferrite from cementite. Nital and picral can be used mixed in a 1:1 proportion.

Oberhoffer's Reagent 500 ml distilled water, 500 ml ethanol, 50 ml hydrochloric acid, 30 g ferric chloride, 1 g copper chloride and 0.5 g stannous chloride. After etching the section should be rinsed in a 4:1 mixture of ethanol and hydrochloric acid. Useful for steels in segregation studies such as arsenic segregation.

Heyn's Reagent 40 ml distilled water and 40 g copper (II) ammonium chloride. Copper precipitates must be wiped from the surface with distilled water or washed off with distilled water from a wash bottle. Useful for phosphorus segregation in steels.

Klemm's Reagent I 50 ml stock solution of saturated aqueous sodium thiosulphate and 1 g potassium metabisulphite. Useful for some colour etching of ferrite and for phosphorus segregation in cast steels and cast iron.

Baumann's Print Solution 100 ml distilled water and 5 ml sulphuric acid. Silver bromide paper is saturated with the solution and firmly pressed against the specimen surface. After 1–5 min, rinse and fix with a solution of 6 g sodium thiosulphate in 100 ml distilled water. Wash and dry. Useful for verification, arrangement and distribution of iron and manganese sulphide inclusions.

Beraha's CdS Reagent 100 ml distilled water, 24 g sodium thiosulphate, 3 g citric acid and 2 g cadmium chloride. Use for 20–40 s. Used as a tint etchant for iron and carbon steels. Ferrite is stained brown or violet. Carbides, phosphides and nitrides may be only lightly stained. With Beraha's reagent, ferrite is coloured, but cementite is not, so that both proeutectoid cementite and cementite in pearlite are in strong contrast to the ferrite, which can make even thin films of cementite easily visible.

Beraha's HCl Reagent I 100 ml stock solution of Beraha I and 1 g potassium bisulphite. Colour etchant for heat-treated steels.

Alkaline Sodium Picrate 2 g picric acid, 25 g sodium hydroxide and 100 ml distilled water. This solution is useful for distinguishing between iron carbide and ferrite in steels. Solution can be heated to boiling but is best used at 50°–70 °C for 10 min or longer if required. The cementite is darkened by this reagent, while ferrite is unaffected. Etching in this solution may provide a good indication of pearlite lamellae spacing.

Beaujard's Reagent 20 g sodium bisulphate and 100 ml distilled water. It is often a good idea to etch in nital for 2–4 s beforehand. Beaujard's reagent can then be used for 10–25 s: the surface should be very carefully washed and dried; otherwise, the deposited surface film will be disturbed. The reagent produces good contrast between ferrite grains and between lightly tempered martensite and ferrite, as well as delineating cementite networks. The reagent works by depositing a complex oxide-sulphide-sulphate film on the metal surface, in various shades of brown.

Dimethylglyoxime Nickel Test Some ancient steels contain nickel as an important impurity. A simple test is to take a nickel print by pressing a blotting paper soaked in dimethylglyoxime against the polished section when the nickel-rich areas are revealed by brown staining on the blotting paper.

Vilella's Reagent 1 g picric acid, 100 ml ethanol and 5 ml hydrochloric acid. A reagent that can be used to reveal clearly the needles of plate martensite. It is useful for exposing the austenitic grain size of quenched and tempered steels if this feature is at all discernible.

Sodium Metabisulphite 100 ml distilled water and 1 g sodium metabisulphite. Colour etchant for heat-treated steels to colour martensite.

Etchants for Copper and Copper Alloys

Acidified Potassium Dichromate 80–100 ml water, 5–8 ml sulphuric acid, 2–10 g potassium dichromate, 4 ml sodium chloride (saturated solution) or a drop hydrochloric acid added just before using.

Ammonium Hydroxide/Hydrogen Peroxide 50 ml distilled water, 50 ml ammonium hydroxide and 10–50 ml hydrogen peroxide. Make up and use fresh only. Adding larger amounts of hydrogen peroxide creates better grain contrast, and adding less hydrogen peroxide creates better grain boundary etching. Can be used with benefit on a number of different alloy types.

Aqueous Ferric Chloride 100 ml distilled water, 5–50 ml hydrochloric acid and 5–25 g ferric chloride. Produces grain contrast, very useful for all copper alloys, etching time from a few seconds to 60 s with 3–5 s being common. The authors prefer to use alcoholic ferric chloride as aqueous solution etches fast and often stains.

Alcoholic Ferric Chloride 240 ml ethanol, 60 ml hydrochloric acid and 20 g ferric chloride. This is the most common etchant used by the authors.

Aqueous Ammonium Persulphate 200 ml distilled water and 20 g ammonium persulphate. Produces grain contrast. Must be use fresh; will not keep.

Acidified Ammonium Persulphate 100 ml distilled water, 10 g ammonium persulphate and 5 ml hydrochloric acid. Helpful etchant for copper-nickel alloys.

Beraha's Lead Thiosulphate Etchant 12 g sodium thiosulphate, 1.2 g lead acetate and 1.5 g citric acid in 50 ml distilled water. Colours grains depending upon their orientation and contrasts α/β-brasses. Can be used after ammonium persulphate pre-etch.

Beraha's Selenic Acid Reagent 300 ml ethanol, 2 ml hydrochloric acid and 0.5 ml selenic acid. Colours grains depending upon their orientation and contrasts α/β--brasses. Can be used after ammonium persulphate pre-etch.

Klemm's Reagent II 100 ml stock solution of saturated sodium thiosulphate and 5 g potassium metabisulphite. Immerse for revealing segregations in cast and worked copper alloys.

Klemm's Reagent III 20–40 g potassium metabisulphite, 100 distilled water and 11 ml stock solution. Colours grains depending upon their orientation. Intermetallics are not etched, and segregations become clearly visible.

Potassium Ferricyanide 5 g potassium ferricyanide and 100 ml distilled water. This etchant can be used to darken some precipitates such as Cu_3P which may coexist with the alpha+ delta eutectoid. Cu_3P can be seen as a purple shade against the very pale blue of the delta phase in bronzes. After etching in alcoholic ferric chloride, this distinction is lost. Some difficulties may be overcome by using a relatively high amount of aqueous ammonia in the final polish.

Etchants for Gold Alloys

Ammonium Persulphate/Potassium Cyanide 100 ml distilled water, 10 g ammonium persulphate and 10 g potassium cyanide. Very useful for gold alloys. Sometimes good results can be obtained after a brief etch/clean in a 10% persulphate pre-etch. The most common problem is etch pitting with this etchant, which can be hard to eliminate.

Aqua Regia 40 ml nitric acid and 60 ml hydrochloric acid. Used for a few seconds or up to 1 min. Use fresh. Aqua regia is a strong oxidizing solution and highly corrosive. In most alloys it provides grain contrast.

Hydrogen Peroxide/Iron (III) Chloride 100 ml distilled water, 100 ml hydrogen peroxide and 32 g ferric chloride. Sometimes useful for variable gold jewellery alloys and Au-Cu-Ag alloys.

Etchants for Silver Alloys

Acidified Potassium Dichromate 10 ml sulphuric acid; 100 ml potassium dichromate, saturated in water; and 2 ml sodium chloride (saturated solution). Dilute 1:9 with distilled water before use and swab with cotton wool. Can also be used without the sulphuric acid addition.

50 ml ammonium hydroxide and 20 ml hydrogen peroxide. Must be used fresh. Immerse for up to 60 s.

25 ml ammonium hydroxide, 25 ml water and 50 ml hydrogen peroxide. For silver-copper alloys. Add peroxide last, use fresh, and sample can be etched for up to 45 s.

Ammonium Persulphate/Potassium Cyanide 100 ml distilled water, 10 g ammonium persulphate and 10 g potassium cyanide. Also useful for gold alloys (see above).

Etchants for Tin Alloys

Ammonium Polysulphide A saturated aqueous solution of ammonium polysulphide. Use for 20–30 min. Wipe off with cotton wool after etching. Can be used for all types of tin alloys. Nital or picral can also be used (see etchants for iron, steel and cast iron).

Taff's Reagent 60 ml ethanol, 30 ml distilled water, 5 ml hydrochloric acid and 2 g ferric chloride. Add one drop of hydrogen peroxide to solution before use. For pure tin and tin-bismuth alloys.

100 ml ethanol and 2–10 ml hydrochloric acid. For pure tin and alloy. Immerse for 1–5 min.

Klemm's Reagent II 50 ml saturated aqueous sodium thiosulphate and 5 g potassium metabisulphite. Immerse for 60–90 s for grain colouration.

Etchants for Zinc Alloys

Zinc alloys are difficult to prepare mechanically. Fake microstructures are common because deformation is difficult to prevent.

Palmerton's Reagent 100 ml distilled water, 20 g chromic oxide, 1.5 g sodium sulphate (anhydrous) or 3.5 g sodium sulphate, hydrated. Can be used for seconds or minutes.

100 ml distilled water and 10 g sodium hydroxide. Can be used for pure zinc and zinc-copper alloys, immersed for 5–15 s.

100 ml ethanol and 5 ml hydrochloric acid. For zinc samples, can be immersed for several seconds.

Klemm's Reagent I 50 ml saturated aqueous sodium thiosulphate and 1 g potassium metabisulphite. Immerse sample for about 30 s.

Etchants for Lead Alloys

If difficulty is experienced in the preparation of lead alloys, a good technique is to try finishing the polishing with fine alumina powder or use etch-polish techniques.

Glycerol Etchant 84 ml glycerol, 8 ml glacial acetic acid,

100 ml ethanol and 1–5 ml nitric acid. Use fresh only. Gives grain boundary contrast. Nital can also be used (see etchants for iron, steel and cast iron).

80 ml water, 15 ml acetic acid and 25 ml nitric acid. For lead and lead-tin alloys. Use fresh for several seconds up to minutes.

Glacial Acetic Acid 15 ml glacial acetic acid and 20 ml nitric acid. Useful for lead solders and Pb-Sn alloys.

Colour Metallography

As compared with conventional etching, colour metallographic methods enhance contrast with interference layers produced by evaporation, by sputtering or by chemical deposition for colour effects (see Chap. 3). It is sometimes useful to investigate the application of colour metallography to ancient metallic object specimens to enhance the visual appreciation of microstructural features. One of the potential advantages to interference film metallography is that coring and segregation may be revealed when conventional metallographic techniques fail. Further colour etching solutions and details concerning the techniques which may be employed can be found in the literature referred to in Chap. 3.

Some of the useful recipes are set out below and in the list of etchants. For colour etching different strengths of Klemm's reagent are the most useful. The stock solution of Klemm's reagents is a cold-saturated sodium thiosulphate solution of approximately 1 kg sodium thiosulphate in 300 ml distilled water, which can be stored without limit. The etchants themselves have to be made fresh every time it is used, by the addition of a few grams of sodium metabisulphite (see above). After immersion etching, you can cover the beaker tightly, or pour the solution into a tightly closed bottle, and keep reusing it for nearly a month – until crystals start precipitating. The stock solution can be taken, and new water can be repeatedly added till the salt will go back into solution. Pre-etching with standard general-purpose etchants such as 10% aqueous potassium peroxydisulphate is often useful but not generally required.

For Beraha's lead sulphide or cadmium sulphide solutions, the conditions of use are more exacting and have to be followed carefully. The chemicals must be dissolved in the order given. After the sodium thiosulphate is dissolved, the lead acetate (or cadmium acetate) is added and allowed to attempt to dissolve. Beraha says that you have to let it go into solution before adding the citric acid, but that does not happen. After about 30 min of stirring, add the citric acid. The solution is then placed in a dark bottle and placed in a dark closed cabinet to age for 24 h before use. This solution will easily last for about 6 months before it starts to change colour and

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is exhausted. It could probably be kept between uses at a temperature of 10–15 °C, but it should be allowed to warm to 25 °C before use. The more common laboratory approach is to mix a stock solution, e.g. 500 ml, of aqueous saturated sodium thiosulphate. Pre-etching is often useful but not generally required.

Beraha's etchants with hydrochloric acid require individual stock solutions and the addition of a few grams of potassium bisulphite before use. The stock solution for Beraha's reagent I is 24 g ammonium difluoride, 1000 ml distilled water and 200 ml hydrochloric acid. The stock solution for Beraha's reagent II is 48 g ammonium difluoride, 800 ml distilled water and 400 ml hydrochloric acid and 50 g ammonium difluoride, 600 ml distilled water and 400 ml hydrochloric acid for Beraha's reagent III.

A Glossary of Terms and Definitions

Acicular structures Non-equilibrium substructure that may possess an elongated or needle-shaped microstructure.

Age-hardening The process of hardening and strengthening of alloys spontaneously or over time at ambient conditions by the precipitation of dispersed particles from a supersaturated solid solution. For the ageing of carbonsteels, see *tempering*.

Allotropy Ability of some elements to change their crystal structure in dependence of temperature or pressure.

Alloy A combination of two or more metallic components. The term alloying suggests that the mixture was deliberate.

Alpha2 phase In ironmeteorites this is a variation of the kamacite crystals, which are the alpha phase in the iron-nickel system. The phase designation means that the crystals are a variation on the usual alpha phase (which here is kamacite).

Alpha brass An alloy of copper and zinc with no more than 38% zinc, usually less than 32% zinc, consisting of a single phase, the copper-rich α_{Cu} solid solution.

Amalgam An alloy of mercury with other metals, which can be liquid, pasty or solid, depending on the proportion of mercury. Mercury may form an amalgam with gold, silver, tin, zinc, lead, copper and most other metals. The microstructure of these amalgams may be complex.

Amalgam gilding Process used for gilding of copper, silver or iron. Gold becomes pasty when mixed with mercury and can be applied to the surface. Gentle heating drives off most of the mercury. Mercury can also be rubbed onto the cleaned substrate surface followed by attachment of gold leaf or foil.

Annealing Process of heat treatment carried out on a metal or alloy, usually to soften the material after cold-working to allow further deformation or to eliminate residual stress. Can be further elaborated as stress-relief anneal, solid solution anneal, normalizing.

Annealing twins Twins that are formed during recrystallization in certain face-centred cubic and also in few body-centred cubic metals. They appear in two

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parallel straight lines across the grain after etching and result from atomic displacements. Twins have a special mirror image orientation relationship to the matrix lattice.

Anode Electrode of an electrolytic cell at which oxidation occurs. In an electrochemical reaction, the anode is the component of a system that usually corrodes.

Austenite Iron undergoes a phase transition between 911° and 1394 °C, from bcc iron to the face-centred cubic (fcc) configuration of gamma iron, called austenite. Austenite can dissolve considerably more carbon, up to 2.03% by weight at 1146 °C.

Bainite Generally a metastable non-lamellar aggregate of ferrite and carbides formed below martensitic start temperatures and above eutectoid decomposition to pearlite. In some nonferrous alloys, microstructures similar to bainite occur.

Bidri Specific Indian zinc alloys, finished by surface treatment to colour it black and often inlaid with silver. The alloys contain high amounts of zinc with small amounts of copper and some lead.

Bloom A semisolid iron extraction process in which a mass of smelted iron and iron slag is produced in the bloomery process. The bloom must be refined by reheating and forging to squeeze out the slag and weld the iron particles to enable a consolidated iron bar.

Body-centred cubic (bcc) A unit cell in which atoms are arranged at the corners of a cube with one atom in the centre of the cube. Bcc metals are strong and tough and can accommodate small atoms within the lattice.

Brass An alloy of copper and zinc, usually with copper as the major alloying element and with zinc up to 40% by weight. Early alloys were binary alloys containing 90–70% copper and 10–30% zinc. The colour of brass changes with increasing zinc content from a rich copper red through pale yellow to white as the zinc increases.

Brazing Joining of metals together with a filler alloy which melts above 425 °C. Modern brazing alloys are usually copper-zinc alloys to which silver is added and therefore often called silver solders. In ancient time copper and copper alloys, silver-gold, copper-silver and the silver-gold-copper alloys were used for brazing operations on iron, copper alloys and precious metals in particular.

Bronze In historical usage, bronze is essentially an alloy of copper and tin. In modern nomenclature, the term bronze includes all copper alloys, which do not have zinc or nickel as the major alloying element, and the composition of the alloy must be specified.

Brinell hardness A static hardness test that uses a small steel ball indenter. This method has become less common but does allow some comparison with the results from the Vickers scale, as well as other scales used more for industrial purposes such as the Rockwell scale.

Carburization Process of increasing the surface concentration of carbon in iron by solid-state diffusion, by heating austenitized iron together with carbonaceous matter such as wood charcoal or horn shavings to produce carbon monoxide gas that is adsorbed by the metal (see also case-hardening).

Case-hardening Synonym for carburization and other diffusional surface treatments but usually involves also subsequent heat treatments like quenching and following tempering of the adsorbed layers.

Casting Fabrication process of pouring metal into moulds of desired shape. After solidification the metal should assume the shape of the mould. The simplest forms are open moulds that are uncovered at the time of casting, but more complex forms have been used from the beginning (see moulds and lost-wax casting).

Casting-on A process of making a cast part attached to an already existing object or component. In antiquity, a lost-wax addition, made by creating a small mould around part of an object and casting on metal directly to it. Often used for dagger handles or repair or construction of large bronze figures.

Cast iron An iron-carbon alloy that usually contains 2–4% carbon. Generally divided into three groups. Grey cast iron in which free carbon occurs as flakes of graphite. It has excellent casting properties and can be machined. White cast iron in which all of the carbon is taken up as cementite and as pearlite. These irons are usually hard and brittle. Malleable cast irons are usually obtained by heat treatment of white cast irons, in the white heart process, for example, a certain amount of carbon is removed from the surface by oxidation.

Cathode Electrode of an electrolytic cell at which reduction takes the place. In many corrosion processes, the cathodic regions are protected during corrosion, while anodic regions are dissolved and electrons flow towards the cathode.

Cementation This term has several meanings in ancient metallurgy. Cementation of gold alloys with salt in a crucible may remove silver leaving pure gold behind. Brass has been made by interdiffusion of zinc vapour to metallic copper, called cementation process. Carbonaceous material may be used to cover wrought iron, which is then heated, so that the carbon can diffuse into the structure (see carburization and case-hardening).

Cementite Hard and brittle iron carbide that crystallizes in the orthorhombic system with the chemical formula Fe_3C containing about 6.6% carbon.

Chasing Non-cutting but plastic deforming metalworking by the use of chasing tools, often of brass, bronze or wrought iron. Softer metals like gold can also be enchased by tools made of antler, wood or bone. Unlike engraving, metal is distorted around the chased design and residual stress is not removed.

Close-packed hexagonal (cph) Close-packed hexagonal metals with a repeating sequence of atoms as ABABABAB. The unit lattice has a hexagonal prism structure with one atom at each corner, one in the centre of the bottom and top faces and three in the centre of the prism. Metals of cph structure tend to be brittle such as cadmium, cobalt, titanium and zinc.

Coherent precipitation Precipitation of fine particles of a second phase, with an orientation that continues the lattice of the matrix. They are usually not large enough to resolve and therefore imperceptible by optical microscopy.

Cold-working Plastic deformation of a metal at a temperature low enough to cause permanent strain hardening. The treatment usually consists of rolling, hammering or drawing at room temperature when the hardness and tensile strength are increased with the amount of cold-work, but the ductility and impact strength are reduced.

Columnar Long column-like grains that can form when a pure metal is cast into a mould. Also seen in electrotyped copper.

Continuous precipitation The formation of precipitates or inclusions from a supersaturated solid solution, distributed uniformly through the grains themselves. They grow by long-range diffusion without recrystallization of the matrix.

Coring Segregation of an alloy on the successive freezing to the solid. Zones are formed, especially in dendritic castings, in which a continuous series of small changes in composition occurs as the dendrite is formed. Especially common, in ancient cast bronzes and cast silver-copper alloys. Coring is accentuated in alloys with a wide separation between liquidus and solidus curves.

Crimping Mechanical joint between two pieces of metal in which they are deformed to shape an overlap or attachment.

Cupel A porous ceramic, usually made from bone ash or a mixture of bone ash with lime. The cupel is used to melt small amount of precious metals, usually silver to separate the lead. In the extraction of lead from silver, the oxidized lead is absorbed into the cupel leaving a button of silver behind. The cupel can then be broken and smelted to recover the lead.

Cupellation A two-stage process applied to extract precious metals, usually silver. Silver can be recovered from argentiferous ores or from debased silver alloys by the addition of lead, which can later be removed by oxidizing the lead in a cupel or in a special furnace, the so-called cupellation hearth.

Cupro-nickel Alloys containing copper and nickel usually from 15% to 70% nickel but in ancient alloys often with less nickel than this. Alloys with about 25% nickel are now used for coinage metals.

Dendritic Crystals formed during solidification and shaped like the branches of a tree. Dendrites are common in cast alloys and may look like an intersecting snowflake pattern.

Depletion gilding Surface enrichment with gold by removal of one or more base components. Commonly used in ancient South America for the gilding of tumbaga alloys or gold-silver-copper alloys by removing copper from the outer surfaces by pickling.

Depletion silvering Silver-copper alloys usually develop a scale when worked and annealed. Removing oxide scale enriches the surface in silver creating a depleted copper zone and making the alloy silver in colour.

Diffusion The migration of one alloy or metal into another. Interdiffusion also occurs with the second metal migrating into the first. Usually heat is required for this process to occur.

Diffusion bonding Bonding or joining of two metals by heating them together. Each will diffuse into the other at different rates creating a strong and permanent metallurgical bond.

Diffusion coefficient The diffusivity D describes the rate of movement of a substance into material. Its value depends on factors like temperature, concentration or crystal structure and is given as an SI unit of square metres per second (m^2/s).

Discontinuous precipitation The formation of precipitates or inclusions from a supersaturated solid solution, laid down at grain boundaries, often by a process of ageing. They grow by short-range diffusion with the recrystallization of the matrix.

Dislocation Defects in the crystal structure of a metal that allow movement of planes or atoms within the lattice. Edge and screw dislocations are two common types.

Dislocation entanglement The density of dislocations increases on working the metal until dislocation entanglement is reached. At this point the metal is brittle, and no further movement can occur. Annealing will restore working properties.

Drawing The act of pulling a wire through a draw plate of hard material to reduce the cross section dimension, with a corresponding increase in length of the wire.

Ductility The ability of a metal to undergo plastic deformation to a certain extend without fracture, especially during drawing.

Electrochemical corrosion Corrosion of a metal in which anodic and cathodic reactions result in metallic dissolution. The most common form of corrosion of buried or marine metals.

Electrochemical replacement plating Electroless plating technology used in ancient Peru as a gilding technique producing layers of extraordinary thinness. Cleaned copper will exchange with gold solutions to form a thin gold surface as the copper is corroded away.

Electrum Naturally occurring or deliberate produced alloys of gold and silver, usually white or pale silvery in colour and containing about 40% silver.

Engraving Cutting metalwork with a sharp graver to remove metal from a surface for decoration. Gravers must be harder than the base metal but also tough to prevent breaking the edge.

Epsilon phase In iron meteorites this is derived from the carbide phase with has the formula $Fe_{2\text{-}3}C$. This is a hexagonal close-packed phase in the iron-carbon system, seen in iron meteorites.

Equilibrium diagram A synonym for a phase diagram or constitutional diagram.

Equilibrium structures Microstructures that represented full equilibrium phases predicted from the phase diagram. In ancient metals the microstructures are usually far from equilibrium.

Equiaxed grain Individual crystal of equal dimensions or properties in all directions. The equiaxed grains are ideally hexagonal in form.

Eutectic The eutectic is a fixed composition in binary alloys with the lowest melting point. The eutectic reaction converts one liquid phase directly into two distinct solid phases upon cooling and the microstructure consists of an intermixture of two or more solid phases.

Eutectoid Decomposition from a solid solution into a finely dispersed mixture of two or more solid phases upon undercooling creates a microstructure called the eutectoid. The eutectoid point is fixed in binary alloys and the morphology may resemble the eutectic.

Fahlore Old German miner's term used for a variety of complex sulphide minerals such as tennantite ($Cu_{12}As_4S_{13}$) and tetrahedrite ($Cu_3Sb_4S_{13}$), chatted with copper ores.

Fayalite An iron silicate (Fe_2SiO_4) which melts at about 1205 °C crystallizes in the orthorhombic system and belongs to the olivin group. Fayalite is the predominant mineralogical constituent of ancient slag. Its name is derived from Fayal Island, which is of volcanic origin and where it has first been observed.

Ferrite Body-centred cubic modification of iron at room temperature, also called alpha iron (α_{Fe}).

Face-centred cubic (fcc) In this lattice system that is an atom at each corner of a cube and an atom at the centre of the cube faces. Face-centred cubic metals tend to be soft and easily worked such as silver, gold, copper, lead and platinum.

Forge welding Basic blacksmithing technology to combine different pieces of iron by heating them to white heat and hammering them to effect an interfacial bond. It is comparable to modern pressure welding.

Fusion gilding A process used in ancient South America, especially Ecuador, for the gilding of copper alloys by dipping or fusion of molten gold alloys to the surface resulting in thick gold alloy coatings. May also be used to create silver alloy coatings over copper.

Gama-hada Japanese decorative technique making use of immiscible metals such as silver or silver-copper alloy droplets on iron.

German silver One synonym for alloys of copper, nickel, and zinc, usually consisting of 52–80% copper, 5–35% nickel and 10–35% zinc. This alloy was formerly used for many decorative purposes as a cheap substitute for silver, since it does not readily tarnish and is also of silvery hue.

Gilded Covering of a less noble metal or non-metal either totally or partially with gold.

Gold leaf Leaf in ancient technology is rare. The term is reserved for gold less than 1 micron thick.

Gold foil Any gold sheet greater than 1 micron thick.

Grain Single crystal with a polygonal shape within a polycrystalline metal or alloy. The interface between two grains, the grain boundary separates areas of the same structure but different orientation.

Grain boundary segregation Also known as grain boundary precipitation, as mostly non-metallic or intermetallic compounds precipitate preferentially at the interfaces because of their higher energy state.

Granulation Usually refers to tiny gold grains attached to an object with a specific solder, made in situ by reduction of a copper salt with organic glue or by use of diffusion bonding of the gold grains.

Graphite An allotropic form of carbon, occurring in the trigonal system as grey, soft, lustrous plates. It is the form of carbon found in steels and cast irons and usually occurs in grey cast irons as thin flakes or nodules.

Grey cast iron Cast iron with a grey fracture. The fracture colour is indicative that the cast iron contains free carbon as graphite.

Gunmetal Copper alloys which may have different compositions, but usually an alloy of copper, tin and zinc.

Hardness Resistance of a material to plastic deformation. Hardness testing is usually performed by the indentation of specified test specimen.

Hard soldering An alternative term for the use of a brazing alloy for joining, as opposed to the use of soft solders.

Hot-working Deformation of metals or alloys above their recrystallization temperature.

Hypereutectic alloy Alloys including a eutectic and having an excess of the solute. The microstructure may contain some eutectic and primary dendrites of the solute.

Hypereutectoid alloy Alloys including eutectoid decomposition and having an excess of the solute. The microstructure may show some proeutectoid precipitations of the solute with some eutectoid.

Hypoeutectic alloy Alloys including a eutectic and having an excess of the solvent. The microstructure may contain some eutectic and primary dendrites of the solvent.

Hypoeutectoid alloy Alloys including eutectoid decomposition and having an excess of the solvent. The microstructure may show some proeutectoid precipitations of the solvent with some eutectoid.

Intaglio The process of engraving or removing metal to create a design. The depression so formed may be filled with niello, glass or enamel.

Interstitial solid solution Some elements (H, C, N) with small atom sizes may occupy lattice spaces between the atoms of a solvent without causing too great a distortion of the original lattice structure.

Kamacite An important constituent of iron meteorites. It is the α(Fe,Ni) phase, an alloy of iron and nickel, usually in the proportions of 90:10 to 95:5 although impurities such as cobalt or carbon may be present. It is a major constituent of iron meteorites (octahedrite and hexahedrite types). In the octahedrites it is found in bands together with taenite, forming Widmanstätten patterns. In hexahedrites, fine parallel lines called Neumann lines are often seen, which are evidence for structural deformation of adjacent kamacite plates due to shock from impacts.

Karat Traditional term used to express the degree of purity or fineness of gold. The fineness of alloyed gold can be expressed in the number of parts of gold that are contained in 24 parts of the alloy or by parts per thousand. For example, 18 karat gold contains 18/20 parts of gold and is 75% gold or 750 parts fine, while pure gold is 24 karat or 1000 parts fine.

Kirkendall effect Phenomenon that can be observed at the interdiffusion of two components having different diffusion coefficients D. Due to the difference in diffusion rate, voids are formed at the boundary interface on the side of the faster component, while the side of the lower component will expand by volume

Leaf gilding Mechanical covering with gold by the application of gold leaf or gold foil. Sometimes held mechanically by roughing the surface or by an organic adhesive.

Ledeburite Name applied to the cementite-austenite eutectic at 4.3% carbon which forms at 1148 °C. During cooling the austenite in the eutectic may transform into a mixture of cementite and pearlite.

Liquidus The line on a binary phase diagram that shows the temperature at which solidification begins upon cooling from the melt or finish melting during heating. In a ternary diagram the liquidus is a surface not a line.

Lost-wax casting Casting metal from a wax model. The object to be made is shaped in wax, either solid or hollow, and is covered in a clay mould. When the wax is molten out, the space can be filled with molten metal, usually bronze or brass.

Martensite Often used for the hard, needlelike component of quenchedsteels, but more generally any needlelike transformation product of a quenched alloy. The most common in ancient materials is martensite in quenched steels or martensite in the beta-quenched bronzes.

Martensitic transformation Spontaneous diffusion less phase change by rapid cooling of specific alloys, like carbon steels or high-tin bronze.

Mechanical twinning Plastic deformation of individual crystals produced by mechanical strain alone, which exhibits changes in orientation of the distorted crystal planes. Twinning occurs in metals with CPH structure such as zinc or bcc metals such as iron.

Meteoritic iron Iron from outer space. Usually an alloy of iron and nickel. Small amounts of cobalt and manganese are typical. Some early exploitation made use of meteoric iron. The iron comes in many different types, the most common being the octahedrites and the hexahedrites.

Moulds Hollow forms made of clay, sand, stone or metal to give molten metals a particular shape. Moulds made of wood and antler have been used for casting tin and lead, while shell of cuttlefish for precious metals is also evidenced. Open moulds are the simplest use of casting into an open-shaped depression in clay or stone. Piece moulds are made of two or more pieces in stone, bronze or clay. Hollow cast objects are usually piece moulds with false cores modelled in clay (see also lost-wax casting).

Neumann bands These are mechanical twins in iron alloys after deformation by a sudden impact. They can often be seen in ancient iron artefacts. In meteorites, they can be found as a series of fine pattern lines seen in cross sections of many hexahedrite iron meteorites and some octahedrites in the kamacite phase.

Nitriding The hardening of steels due to nitrogen content that may result in nitrides or carbon nitrides being formed in the alloy, usually of acicular shape.

Pattern-welding Ancient blacksmithing process of ornamenting a metal surface with a specific pattern by welding different irons and steels together. Forge-welded composite rods of iron and steel can be twisted and combined with other composite rods to produce complex manifold pattern after grinding, polishing and probably final treatment with acids.

Pearlite A fine mixture of ferrite and cementite found in steels. The eutectoid, pearlite, will be complete when the carbon content reaches 0.8%.

Peritectic Reaction of a solid phase with a liquid of a different composition to create a new solid phase by cooling to the peritectic temperature. The new phase may consume all of the liquid to form a totally new solid. An example is the beta phase in the bronze system.

Peritectoid Solid-state reaction in which two solid phases in a binary system react to form a new solid phase. A peritectoid reaction occurs in the bronze system, for example, in which at 65% copper, a reaction between Cu_3Sn and the solid solution gamma produces a new phase, Cu_4Sn at about 580 °C.

Pewter Ancient pewter is an alloy of lead and tin, much used in Roman times. The poisonous nature of lead has resulted in the replacement of lead with antimony, although antimony is also inadvisable in high amounts for utensils. Pewter in antiquity may consist of 60–80% tin and 40–20% lead, while modern pewter may be 15–30% copper, 5–10% antimony and 87–94% tin.

Phase A component in a heterogeneous system having a homogeneous chemical composition and uniform physical properties.

Phase diagram A diagram with axes of temperature and composition describing the different phases that may occur in an alloy with change in either composition or temperature. A binary phase diagram consists of two components on each end of the horizontal axe versus the temperature on the vertical axe. A ternary diagram consists of three components plotted on a triangle, representing each the horizontal axe of a binary diagram, while the temperature is plotted perpendicular to composition triangles.

Piece mould A mould taken from a model that may be assembled in a number of pieces before being used for sloshing wax over the mould interior for lost-wax copies of a master model. Such techniques were common in the Renaissance.

Plessite A fine mixture, a eutectoid, between kamacite and taenite (qv), the alpha and gamma phase of the iron-nickel system. It is found in the octahedrite meteorites, and many morphological varieties are known to occur. It is a meteorite texture consisting of a fine-grained mixture of the minerals kamacite and taenite found in the octahedrite iron meteorites. Some varieties are acicular plessite, black or type II plessite, comb plessite, net plessite, pearlitic plessite and spheroidized plessite.

Polycrystalline Consisting of many individual crystalline grains. Most metal are polycrystalline solids.

Polygonal Many-sided. Some grain shapes may be polygonal.

Prill In the extraction of copper from primitive smelts, the metal is produced as small droplets or particles in a slaggy matrix. These small metallic particles are called prills which often are extracted by breaking up the melted product and salting the metal. In a crucible process trails all small droplets of metal adhering to the crucible lining.

Pseudomorphic The replacement in the corrosion process of one material with corrosion products of another that mimics the form of the replaced product. Pseudomorphic replacement of organic materials is common on iron and can occur with copper alloys and silver-copper alloys as well.

Puddled iron Process to refine pig iron by stirring the liquid iron with long rods (paddle) to bring all iron into contact with the hot air to oxidize as much impurities as possible. The technology has been developed in England during the eighteenth century and spread all over Europe in the nineteenth century. It has finally given up at the beginning of the twentieth century because of the introduction of the Thomas process.

Quenching The act of quickly cooling a metal or alloy by plunging it into a cold liquid like water, oil or brine to supress equilibrium decomposition. The quenching of steel refers to the production of martensite and bainite to harden a tool or weapon. Quenching of nonferrous alloy is used to avoid embrittlement during cold-work. The quenching of gold alloys is to suppress ordering reactions, while silver-copper alloys or bronzes are quenched to prevent eutectic and eutectoid decomposition, respectively.

Repousse Working from the back of the metal, often using the slight relief of a chased design on the front. The metal is then displaced by hammering, usually on a soft support such as pitch, so as to create raised designs on the front.

Riveting Joining of metal sheet by small metal pegs passing through the sheet and being hammered down.

Safidruy Islamic term for high-tin bronzes, often white in colour.

Shakudo Japanese term for the deliberate use and manufacture of coloured gold-copper alloys.

Shibuichi Japanese term for decorative silver-copper alloys often worked and annealed, to create decorative surfaces when coloured by chemical etching or staining.

Sinking A technique in which a vessel can be produced by hammering from the inside. The sheet metal is hammered either on the flat surface of an anvil or more commonly hammered into a shallow concave depression in the anvil. Also called blocking or hollowing.

Slag A relict of pyrotechnical processes like smelting or processing metals, consisting basically of silicates and metal oxides. Slag can contain metallic prills, charcoal and undecomposed ore minerals. Slag can be entirely glassy like early blast furnace slag, but most ancient slag is a mixture of high-temperature minerals like fayalite, glassy components and secondary minerals from the weathering of the slag.

Slag stringers Small pieces of slag that have become incorporated into the metal and are then strung out as small elongated ribbons as a result of working the metal to shape it.

Slip planes Dislocated crystallographic planes in which slip occurs due to plastic deformation. Slipping can only occur in certain crystal planes and can only move in specific directions. Due to the different atomic arrangements in the distinct crystal systems, dislocations move along a given system. Especially fcc metals may show a fine series of parallel lines called slip bands, because of their 12 slip systems.

Slush casting Method of casting in which metal is often spun or agitated in the mould so that a thin shell is formed. More common in ancient and historic metalwork is slush wax work in which wax is slush cast over a piece mould interior before investment.

Soft solders A term predominantly applied to lead-tin alloys used in ancient soldering. The upper limit of the melting range of modern solders is about 425 °C, but ancient solders melt at about 130–260 °C.

Solid solution A relative homogenous crystalline phase of different elements which share the lattice of a matrix metal. Substitutional and interstitial solid solutions are possible.

Solidus The line in the phase diagram that separates the pasty stage of the alloy, usually a mixture of solid and liquid, from the completely solid alloy below the temperature of the solidus line. The solidus temperature may be different at different alloy compositions, depending on the type of the phase diagram.

Sorbite An obsolete term for very fine pearlite produced by the decomposition of martensite by tempering or insufficient quenching.

Speculum A name sometimes applied to Roman or bronze mirrors containing a high percentage of tin. Historic speculum may contain about 67% copper and 33% tin. Ancient mirrors made use of similar alloys often of beta bronze composition and up to about 24% tin.

Spinning Turning metals on a lathe followed by depression of metal while in motion.

Stamping Plastic deformation of metal by a hard die, often used for assay purposes.

Steel A malleable alloy of iron and carbon that contains about 0.1–1.9% carbon. The carbon is present as cementite, usually as a component of pearlite.

Sterling silver A common coinage binary alloy of 92.5% silver and 7.5% copper.

Strain hardening A synonym for work hardening.

Strain lines Same as slip lines.

Striking A method of making coins and medals. The impression is cut in negative in a very hard material, and this die is then placed over the coin blank and given a heavy blow, thus compressing the metal of the blank into the recesses of the die.

Taenite An important phase constituent of iron meteorites; it is (gamma) γ (Fe, Ni), a solid solution alloy of iron and nickel. The amount of nickel present in this phase varies from about 20% up to 65%. In octahedrites (a class of meteorites), it is found in bands interleaved with kamacite, making the well-known Widmanstätten pattern, whereas in ataxites, it is the dominant constituent. In octahedrites a fine intermixture with kamacite can occur, which is called plessite.

Tempering A heat treatment that is usually applied to steels in which some of the hardness is removed by heating at moderate temperatures from 452 to 650 °C depending on the type of tempering required. Tempered martensite decomposes and forms fine particles of iron carbides.

Tinning The operation of coating a base metal with tin. The coating may be obtained by hot dipping into molten tin or by wiping the molten tin over the surface of the object.

Troostite An obsolete term for very fine pearlite, not resolvable by optical microscopy. It is produced by the decomposition of martensite by tempering or insufficient quenching and is sometimes synonymous with bainite. Nodular troostite is very characteristic for steels not cooled quickly enough to form martensite.

Tumbaga Collective name given in ancient South America to the alloys of copper and gold, of wide range of composition and colour.

Tutenag Copper-zinc-nickel alloy of silvery colour, imported from China to Europe in the eighteenth to nineteenth century AD.

TTT diagrams Time-temperature-transformation diagrams most useful in considering the nature of the quenched microstructure to be found in steels and high-tin bronzes. The quenching rate and composition results in a different series of TTT diagrams that are commonly used to investigate transformation effects on components found during the quenching of alloys.

Vickers hardness A static hardness test that uses a pyramid-shaped diamond indenter having an angle of 136 degrees between the faces. The loading can be used for microhardness measurements for all materials. It is one of the most useful hardness testing scales.

Weld A term used to describe a joint made between two metals made by the heating and joining the separate parts with no solder applied. Ancient welds were often made in precious metals, such as gold and silver and in the joining of iron components, especially in the fabrication of wrought iron.

White cast iron Cast iron with a whitefracture due to the presence of the carbon in the cast iron as cementite rather than free graphite.

Widmanstätten structure A very characteristic type of structure that forms when a new solid phase is produced from a parent solid phase as plates or laths along certain crystallographic planes of the original crystals. The structure is associated with many meteoric irons and with changes upon cooling in worked iron and many nonferrous alloys.

Wootz A kind of steel, made in small crucibles in ancient India and often of hypereutectoid steel with a very low slag content. This cast steel was widely used for the manufacture of sword blades and other quality products.

Work hardening Increase of hardening by plastic deformation.

Wrought The process of hammering or deforming a metal or alloy, as opposed to casting.

Wrought iron Malleable**i**ron that has been produced from the bloomery process and has been consolidated by hammering and annealing into a wrought product. Wrought iron usually contains slag stringers that have been elongated and flattened in the process of working from the bloom.

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D. A. Scott, R. Schwab, *Metallography in Archaeology and Art*, Cultural Heritage Science, https://doi.org/10.1007/978-3-030-11265-3

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