

### Introduction

Metals and related materials provide a great deal of information on the ways in which they were manufactured and used. Some of this information can be gained from a simple visual examination of the objects. Supplementary information can be gained through a consideration of the chemical composition of the material (e.g. metal alloy type, impurities, etc) and some from the examination of the structure of the materials at a microscopic level.

### General considerations

Almost all materials are crystalline but in most cases the crystals are too small to be visible to the unaided eye. In many cases a material which appears homogeneous to the naked eye is actually composed of two or more different materials. The use of microscopes reveals the size, shape, orientation and distribution of crystals in a metal or other material. Microstructure influences physical properties and two metals with exactly the same chemical composition but different microstructures may have quite different properties. The distribution of crystal orientations (texture) of a sample may be random or there may be some preferred orientation. Texture is seen in many materials, especially in forged metals, and can have a great influence on physical properties. The examination of microstructure (metallography) can provide important information on the way in which a metal was cast, heated, cooled and forged. Metallography can yield clues which will allow the reconstruction of the sequence of actions employed in the fabrication of an object.

The most ancient materials are not homogeneous. Before the 18th century it was rare for ferrous alloys to be melted and so they retain quantities of slag as well as an uneven distribution of alloying elements, particularly carbon and phosphorus. Non-ferrous alloys often show some variation in the concentration of certain elements through the thickness of the casting. They also retain some non-metallic inclusions, including oxides and sulphides. All alloys can show depletion (or enrichment) of elements at the surface following oxidation, either during manufacture or due to post-depositional corrosion. The heterogeneous nature of most materials means that a comprehensive estimation of their microstructure requires a substantial sample. In most cases, the ideal metallographic sample is one which provides a cross-section through the entire artefact.

The removal of substantial sections of an artefact is, of course, destructive and raises ethical issues which must be resolved through a dialogue between all parties (archaeologists, curators, scientists, etc). Sampling should, wherever possible, result in the least possible damage to the artefact. The likely damage to the artefact should be weighed against the likely increase in scientific knowledge. Balancing curatorial and research interests is best achieved through a written statement of aims, objective and methods.

### Metallographic methods

Metallography requires the removal of small samples, which are then mounted in a suitable resin and polished to a

mirror finish. The microstructure of some metals may be immediately apparent with the aid of a metallurgical microscope, but in many cases some of the microstructure will only be revealed once the polished surface has been etched using suitable reagents. The etchants will commonly indicate the boundaries between individual crystals (or grains) which will show the size, shape, orientation and distribution of a particular material or phase in the sample.

Metallographic samples are usually observed using an optical microscope, i.e. the sample is illuminated using light and the image of the sample is magnified using high quality glass lenses. Images of the microstructure can be recorded using digital cameras, and the microstructure can be analysed using appropriate software tools (e.g. to measure grain size and orientation). The resolution of microscopic details is limited by the wavelength of light – details smaller than the wavelength of light (~1 micron, or one thousandth of a millimetre) cannot be imaged.

High resolution microscopy can be achieved using electron microscopes as the illumination is provided by electrons with a much smaller wavelength than light. Where an electron microscope is fitted with a suitable X-ray fluorescence detector, it is possible to carry out chemical analyses and these may be carried out on small discrete crystals and inclusions within the sample. Electron microscopes may also be fitted with back-scattered diffraction (BSD) detectors which provide information on grain orientation and texture.

The metallographic examination of metals can also be supplemented by hardness testing. The hardness of a metal (this property is related to strength) can be determined using an indentation technique. A small diamond is pressed into the surface using a defined load: the width of the impression is inversely proportion to the hardness and strength.

### Metallography in archaeology

The most frequently examined metals in archaeology are iron (and its alloys) and copper (and its alloys). The metallographic examination of other metals from archaeological contexts is rare. The nature of the microstructures observed in these two groups of metals are quite different and reflect their underlying crystal structure and physical properties.

### Ferrous alloys

Most iron (ferrous) alloys have very high melting temperatures and so were largely produced using a solid state reduction process. During smelting the ore was reduced to a metal but this occurred below the melting temperature of the metal. At times this results in an extremely heterogeneous microstructure. Different ferrous alloys can be produced depending on the nature of the ore and smelting technology. A common iron product comprises simple grains of more-or-less pure iron (ferrite). If the iron has been forged at relatively low temperatures then many of the individual grains will have a preferred orientation. The grains will be elongated in a plane perpendicular to the direction of forging. More commonly

iron is forged at a sufficiently high temperature that the crystals can reform with no preferred orientation.

Most ferrous alloys contain non-metallic inclusions. These are usually composed of iron and other oxides and may have different origins. At least a proportion of the non-metallic inclusions derive from slag produced during the initial production (smelting) of the metal. At the iron was formed below its melting temperature, the separation of metal and slag would be imperfect and some smelting slag would remain trapped inside the metal. Other non-metallic inclusions may be formed (in part at least) through reactions with fuel ash in the blacksmith's hearth or with fluxes used by the blacksmith. The size, shape, orientation and distribution of non-metallic inclusions show how the artefact was wrought.

Ores rich in phosphorus will tend to yield an iron-phosphorus alloy. The identification of iron-phosphorus alloys is possible using specialised metallographic etchants but sometimes it is surmised when the hardness values are higher than would otherwise be expected. Where possible the presence of phosphorus should be tested using a technique of chemical analysis.

When smelting is carried out under very reducing conditions the metal will tend to be an alloy of iron and carbon (steel). Steels may also be formed by carburising a plain (ferritic) iron. The plain iron would be packed with carbon (e.g. charcoal) and then heated to allow the carbon to diffuse into the iron. The identification of steels is easily achieved using metallographic techniques. At room temperature carbon has almost no solubility in iron and so when present tends to form iron carbides (cementite). These are usually present as long thin plates alternating with pure iron (ferrite). When seen in cross-section at low to moderate magnification the ferrite-cementite pattern has an almost iridescent quality giving rise to the label pearlite. The carbon content of bloomery iron was often rather variable, even across rather small distances. The carbon content of carburised iron would tend to be greatest at the surface and gradually decrease towards the centre of the object. The carbon content of steels may be low (usually 0.1–1%) but this can have a profound effect on the physical properties of the metal.

The material properties of steels are further enhanced by heat treatments which are readily apparent using metallographic techniques. If a carbon steel is rapidly cooled by plunging it in water a new microstructure is formed – martensite. The carbon, which was not soluble in iron at room temperature, is soluble in red-hot iron but rapid cooling retains the carbon in solution. Metallographically, martensite has a distorted structure with the appearance of fine needles (acicular). Physically, martensite is extremely hard but also rather brittle. The hardness and brittleness of martensitic steels may be moderated by tempering: the quenched metal is reheated which allows the release of some of the carbon from solid solution.

The manufacture of iron artefacts is greatly facilitated by the relative ease with which two ferrous alloys may be joined by forge welding. Two pieces of iron (or iron alloys)

that have been heated sufficiently may be joined together by simply hammering them together. The line of a forge weld will usually be visible metallographically as a distinct line: on either side the microstructure and the metal composition may be different.

Forge welding was widely used to combine different ferrous alloys into composite artefacts. Edged tools and weapons were often formed by welding a steel edge to a plain iron back or core. Techniques for combining different alloys may have important cultural implications. For example, in many Saxon knife blades a steel edge was butt welded to an iron back, whilst Anglo-Scandinavian smiths favoured 'sandwiching' the steel between two low carbon sides.

### Copper alloys

Copper has a lower melting temperature than iron and would usually be molten during production. In addition the crystalline structure of copper means that the solidification of the copper will be readily apparent metallographically.

As copper cools and makes the transition from a liquid to a solid the first portions to solidify form tiny dendrites (tree-like formations). Each crystal will contain a dendrite. The dendritic formation will usually be visible under a microscope but is enhanced if the copper contains even minute proportions of alloy elements (tin, zinc, arsenic, etc) and is etched using suitable chemicals.

Hammering will tend to squash the crystals and the dendrites flat. In addition the crystals will increasingly contain fine striations or strain lines. As the metal is hammered it become harder and harder and this is visible metallographically as more and more strain lines. The work-hardened metal could be returned to a softened state by reheating; this would remove all of the strain lines and produce new crystals (it would also tend to remove the residual dendritic effects).

Copper alloys could not be forge welded but could be soldered using small quantities of an additional metal with a low melting temperature. Surface treatments such as gilding, silvering and tinning were all used in antiquity. Metallography can identify the method used to apply the coating by examination of compounds formed between the two dissimilar metals.

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