THE METALLOGRAPHIC EXAMINATION OF ARCHAEOLOGICAL ARTIFACTS

Laboratory Manual

MIT
SUMMER INSTITUTE IN MATERIALS SCIENCE AND
MATERIAL CULTURE

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CONTENTS

METALLOGRAPHY

Metallography is the study of the structure of metals and of metal alloys through the examination of specimens with a metallurgical microscope. The structures observed in the microscope are often recorded photographically.

The metallographic study of an archaeological artifact involves the removal of a small sample of metal from the artifact and the subsequent microscopic examination of the sample.

Types of information about an artifact obtainable through metallography

1. the fundamental processes by which the object was manufactured, e.g. cast in a mould or worked to shape; cast and subsequently worked; soldered or welded together; cast solid or hollow, etc.;

2. the temperatures to which the metal may have been subjected during or after manufacture (including casting and annealing temperatures; tempering and quenching ranges);

3. the presence and nature of surface decoration and coatings and the existence of joins, e.g. gilding or silvering; inlays; soldering or welding;

4. an idea of the composition of an alloy, e.g. the % of carbon present in steel, or the % of tin present in a tin bronze;

5. the type and extent of internal and external corrosion.

Sample selection

The decision about where a sample should be removed from an object and how large the sample may be should be made so that maximum information is obtained from the smallest possible sample. On the other hand, the sample must be large enough so that the information obtained is representative of the whole. Occasionally it is possible to take multiple samples from an object or even to cut the object into several pieces. Often, however, only a single sample may be removed from a given artifact.

The location of the sample is crucial in reconstructing the production history of the object. For example, if an object has been assembled from many individual pieces of metal, the sample might be taken at the location of a join to determine if the join is mechanical or a soldered or welded join; if the object has a surface coating of metal different from the metal of the matrix, the sample might be removed so that it includes both surface and underlying matrix metal, to explore the nature of the bond between the

two; if the object is a tool with a cutting edge, the sample might be taken from the edge to determine how it was shaped or sharpened and if it was hardened locally to withstand use.

The choice of location of the sample reflects the questions that the metallographer poses about the object and that he or she hopes examination of the sample will answer. Since the structure of the metal within a given artifact may vary from place to place--depending upon how different parts of the artifact were treated during its manufacture or use--it is advantageous to remove samples from those locations on an object where important structural differences are thought to exist. In this way the interpretation and comparison of the structures can lead to the fullest reconstruction of the history of manufacture and use of the object.

Principles of metallographic examination

Metals and alloys are polycrystalline, that is, they are composed of crystals commonly referred to as grains. The size, shape, and configuration of the grains within a metal or an alloy are a function of the way in which the metal was produced and used. The metallographic examination of specimens allows the metallographer to observe and record the crystalline structures and to interpret from them the history of manufacture and use of the material.

Metals and alloys often contain features other than grains. Such features include pores (from the evolution of gases and the formation of bubbles in liquid metal as it solidifies in a mould); non-metallic inclusions such as oxide or sulfide particles or bits of slag in the metal; fissures or other flaws that may arise when the metal shrinks and cracks upon cooling; surface and internal corrosion products, and so forth.

All these features have meaning and must be observed and recorded. For each feature, one normally records the following characteristics:

-shape

-size

-color (in plane polarized light or with crossed polars)

-distribution

Some features--such as voids, cracks, non-metallic inclusions, corrosion products--are often visible upon microscopic examination of the highly polished surface of the metal sample. This is known as examination of the metal in the <u>as-polished condition.</u> To reveal the grain structure, however, the metallographer must etch the metal--subject it to corrosive attack by selected reagents--before microscopic examination can ensue. This is known as examination of the metal in the <u>etched condition</u>. Both types of examination are essential in the study of archaeological artifacts.

<u>General procedures for the metallographic examination of archaeological artifacts</u>

We may summarize the steps necessary for sample preparation, as follows:

1. removal of the sample from the object;

2. mounting of the sample in a small block of material--usually a plastic--so that it may be held easily;

3. grinding the specimen surface flat;

4. polishing the specimen surface to a scratch-free condition;

5. examination of the as-polished surface of the specimen with the metallographic microscope to observe features such as voids, corrosion, and chemical inhomogeneity of the metal;

6. photographic recording of the as-polished features;

7. etching of the sample surface with a suitable etchant, chosen according to the composition of the metal (e.g. copper, tin bronze, steel, etc. will each call for a different set of etchants);

8. examination of the etched surface of the specimen with the metallographic microscope;

9. photographic recording of the etched structures.

The techniques of specimen preparation, examination, and interpretation may be found in basic texts on metallurgy and metallography. The bibliography included in this manual lists some of those texts, and notes on some of the procedures are included in the manual.

METALLOGRAPHIC SAMPLING OF ARCHAEOLOGICAL ARTIFACTS

There are often severe restrictions on the quantity of metal that can be removed from an artifact for metallographic examination. On the other hand, even a very small sample, smaller than a pin-head if necessary, can be mounted and polished for examination, although great care has to be exercised at all stages of preparation. It is much easier to work with somewhat larger samples--samples the size of a grain of rice--unless entire artifacts or substantial fragments are available for sectioning. There are a number of considerations and procedures that must be followed during the sampling stage of analysis:

1. The object should be photographed or drawn before the sample is taken.

2. The sample should be representative of the object as a whole or of a selected feature or area of the object.

3. The exact location on the object of the site of the sample should be indicated on a drawing of the object.

4. The microstructure of the sample should not be altered in the process of its removal from the object. That is, anomalies in the grain structure must not be introduced through incorrect sampling procedure.

5. The sample should be assigned a laboratory number together with sufficient documentation to ensure that its identity will be preserved.

The nature of the object itself may dictate how or where a suitable metallographic sample can be removed. For example, it may have to be taken in as unobtrusive a location as possible, or a small fragment removed from a broken edge may be the only allowable sample. It is often difficult, therefore, to ensure that a fully representative sample is available; nevertheless, there is usually much useful information to be gained from the sample concerned.

Sampling procedures

A number of procedures are available for the removal of samples from artifacts. The appropriate method will depend upon the size and condition of the object as well as upon its uniqueness: a unique object may never be sampled, whereas an object that is one of hundreds may be sampled liberally.

1. A <u>hacksaw</u> with a fine-toothed blade can be used to cut large samples. If the amount of heat generated in cutting becomes excessive, the original microstructure of the sample may be altered. The blade can be periodically cooled in water or ethanol to prevent excessive heating through friction. The removal of the sample will entail considerable loss of solid as fine powder. This powder may be kept for chemical analysis although it may not be completely free from contamination.

2. A fine <u>jeweler's saw</u> may be employed. Different types of saw blades are available with progressively finer teeth. They are easily broken if they become wedged awkwardly in the cut being made, thus care has to be taken in the selection of a blade which is sufficiently robust for the job in hand. It is possible to remove very small specimens quite accurately, often with minimal damage to the object concerned. If enough powdered metal is produced, it may be kept for chemical investigation.

3. A <u>core drill-bit</u> can be used. The hollow bit drills into the object and removes a cylindrical core of metal which can then be mounted for examination. This technique may sometimes allow a metallographic sample to be taken in circumstances impossible with any other method.

4. A <u>wafer blade</u> can be used to cut a thin slice or remove a small 'V' shaped section from the object. The cutting blade is often an oil-cooled metal disc impregnated with diamond powder around its circumference. Other thin wafer blades are made of steel and can be attached to a small, hand-held, electric drill.

MOUNTING AND PREPARATION OF METALLOGRAPHIC SPECIMENS

Once the sample has been removed from the object, it must be mounted and prepared for examination with a metallurgical microscope. Before mounting, all oil and grease should be removed from the sample by washing it in acetone or ethanol, then drying it.

Mounting the sample

Each sample is mounted by placing it in a mould--usually cylindrical in shape--and filling the mould with a suitable material that embeds the sample and holds it firmly during the grinding and polishing operations that ensue.

Two kinds of mounting procedure may be used: cold mounting and hot mounting. Cold mounting involves use of synthetic resins--such as epoxy, polyester, and acrylic resins-- that are introduced into the mould and cure or harden at room temperature. These plastic materials embed the sample and are often transparent. When hard, if their surfaces are polished, it is easy to see the sample inside the mount. In hot mounting, the mould is filled with a synthetic powdered material that liquifies and embeds the sample when the mould is heated and subjected to a moderate pressure. Special devices, known as mounting presses, are needed for this operation. The mounting material is usually opaque, but it is often considerably harder, when set, than the cold-mounting resins. On the other hand, care must be taken that the temperature needed to melt the mounting powder will not be so high as to alter the structure of the metal sample.

When a sample is very small, some device may be necessary to hold it in its proper orientation within the mould until the embedding material has solidified.

Grinding

Once the sample has been mounted, the resin block must be ground flat. The standard procedure at this stage is to use wet silicon carbide papers with grit sizes progressively finer from 120 grit to 600 grit. Intermediate stages are 240 and 400 grit. The sample must be held so that it does not rock or move out of a single grinding plane, otherwise severe difficulty in obtaining an optically flat surface will be experienced later. Starting with the coarsest grit paper, the sample is moved backwards and forwards over the paper until a uniform ground finish is obtained. It is then carefully washed under running water, examined, and returned to the next grade of paper, rotating the sample through 90^{0} before grinding recommences. This process is repeated for the subsequent grinding papers, rotating the specimen through 90^{0} on each paper. It is very important completely to eliminate the scratches from the previous grinding stage otherwise they will not be removed in polishing.
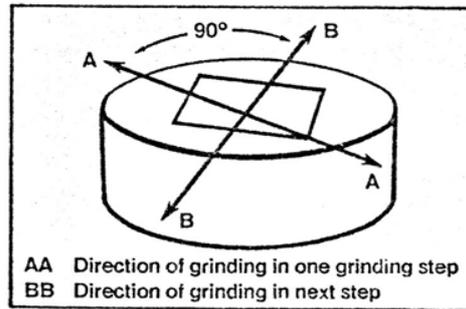
Rotate the mount through 90° on each
successive grinding paper

Polishing

The best results for most ancient metals are obtained by polishing on diamond-impregnated rotary polishing wheels lubricated with a mineral oil. The diamond powders are usually supplied as tubes of paste. The usual range of diamond powder sizes are: six micron, one micron, and one-quarter micron. Some of the polishing can be carried out automatically using a variety of machines or polishing attachments. Hand-finishing, however, is usually preferable for best results on one micron or one-quarter micron diamond paste. Polishing with diamond powders produces less rounding of surface details than is apparent when using a-alumina, y-alumina, or magnesium oxide pastes.

Polishing is carried out by holding the specimen against the rotating polishing cloth. It is difficult to specify how much pressure must be used: too little pressure retards the rate of polishing and may result in some pitting of the surface; too much pressure may distort the surface. The correct polishing pressure varies with different metals and can only be learned through practice.

After initial polishing on six micron diamond paste, the sample should be washed in water, rinsed in ethanol or acetone and dried. It can then be polished on one micron diamond for at least 5 minutes. For many routine purposes this is sufficient and the sample should then be carefully washed to remove all traces of polishing compound and oil before it is ready for examination with the metallurgical microscope. For very high quality work, finish by final polishing on one-quarter micron diamond.

To minimize directional polishing effects, the sample should be rotated in a direction opposite to that of the wheel rotation.

The direction of rotation of the sample during polishing

ETCHING METALLOGRAPHIC SPECIMENS

In most cases, an etching reagent is needed to develop the structure of a metal sample so that the structure can be examined with a metallurgical microscope. The etchant usually attacks the boundaries that separate one grain from another so that the grains of the polished section can be distinguished and their size, shape, and orientation studied.

Before etching, the surface of the polished sample must be cleaned of all grease, oil, and remains of polishing materials. A small amount of the etchant solution is poured into a small petri dish. The mounted sample may then be immersed in the solution for a prescribed period, or a cotton swab may be saturated with the solution and rotated gently on the polished metal surface.

After etching, the sample is washed and dried. Soap and water are adequate for washing, and ethanol or alcohol may be used for rinsing. Drying is usually carried out with a hand drier such as is used for drying hair.

Etched samples should always be stored in a sealed desiccator to keep them dry. Etched metal surfaces are highly reactive and can tarnish rapidly in the air, especially under conditions of high humidity. Once etched, the surface of the specimen should never be touched by hand.

Each metal or alloy system calls for a particular group of etchants for the development of microstructure. Some of the more common etchants useful for the kinds of metals and alloys normally encountered in the examination of archaeological artifacts are listed in a separate section of the manual.

COMMON ETCHANTS FOR COPPER, COPPER ALLOYS, IRON, STEEL AND SILVER

Etchants for Copper and Copper Alloys

Etchant	Composition		Use
Ferric nitrate	$Fe(NO_3)_3 \cdot 9H_2O$ HCl H_2O	5 g 25 ml 70 ml	Good for bringing out grain boundaries. A clean Etchant. Rarely stains sample. SWAB..
Potassium dichromate	$K_2Cr_2O_7$ Saturated NaCl solution H_2SO_4 H_2O	2 g 5 ml 8 ml 100 ml	Good for bringing out grain boundaries. Will stain at times. Often followed by $FeCl_3$. SWAB.
Potassium dichromate plus HCl	$K_2Cr_2O_7$ Saturated NaCl solution H_2SO_4 H_2O HCl	2 g 5 ml 8 ml 100 ml 1-3 drops	Slightly stronger than the standard dichromate Etchant. SWAB.
Ferric chloride	$FeCl_3$ HCl H_2O	10 g 30 ml 120 ml	Good for revealing gradients in composition (e.g. coring and segregation); gives contrast following dichromate etch; SWAB. ETCH LIGHTLY OR BY SUCCESSIVE LIGHT ETCHES TO REQUIRED RESULT. SOMETIMES DILUTION NECESSARY.

Etchant	Composition		Use
Alcoholic Ferric chloride	$FeCl_3$	5 g	SWAB.
	Ethyl alcohol	96 ml	
	HCl	2 ml	
Ammonium hydroxide-hydrogen peroxide	NH_4OH	5 parts	Peroxide content varies directly with copper content of alloy to be etched. IMMERSE OR SWAB FOR ABOUT 1 MIN. Fresh H_2O_2 desirable for good results.
	H_2O	5 parts	
	H_2O_2	2 to 5 parts	

(Continued on next page.)

Etchants for Silver and Silver Alloys

Etchant	Composition		Use
Dichromate	$K_2Cr_2O_7$ (saturated solution)	100ml	Use 1 part:9 parts H_2O Wash well after use.
	$NaCl$ (saturated solution)	2 ml	
	H_2SO_4	10 ml	
Potassium cyanide-ammonium persulphate	KCN (5% solution, by weight)	1 part	Stock separately. Mix only when needed for etching. Use in exhaust hood, as fumes are highly toxic.
	$(NH_4)_2S_2O_8$ (5% solution, by weight)	1 part	Addition of 2% KI will produce more attack.

Etchants for Iron and Steel

Etchant	Composition		Use
Nitric acid (nital)	HNO_3 Ethyl or Methyl alcohol	1-5 ml 100 ml	Etching rate is increased or selectively decreased with amount of HNO_3. SWAB for a few second to 1 min. In carbon steels: (1) to darken pearlite and give contrast between pearlite colonies; (2) to reveal ferrite boundaries; (3) to differentiate ferrite from martensite.
Picric acid (picral)	Picric acid Ethyl alcohol	4 g 100 ml	More dilute solutions occasionally useful. SWAB for a few seconds to 1 min. or more. Does not reveal ferrite grain Boundaries as readily as nital. Use for all grades of carbon steels.

Suggested Etchants for Copper-Arsenic Alloys

For approximately 0.5 % As:

    A mixture of:
        10 ml NH$_4$OH
        2 ml H$_2$O$_2$ 3% solution

Swab for 5-10 seconds

For 1.0-7.0 % As:

    A mixture of:
        10 ml NH$_4$OH
        2 ml H$_2$O$_2$ 3% solution

Swab for 1-3 seconds, followed by:
    A mixture of:
        10 ml HCl
        1 drop H$_2$O$_2$ 30% solution

Immerse for 3-10 seconds.

For 10.0-13.0 % As:

    A mixture of:
        10 ml HCl
        10 ml Acetic acid
        5 drops H$_2$0$_2$ 30% solution

Immerse for 5-10 seconds.

PRINCIPLES OF THE METALLURGICAL MICROSCOPE

Bright-field illumination

Metallurgical microscopes differ from biological microscopes primarily in the manner by which the specimen is illuminated. Unlike biological microscopes, metallurgical microscopes must use reflected light. Figure 1 presents a simplified ray diagram of the illuminating and imaging system of a metallurgical microscope.
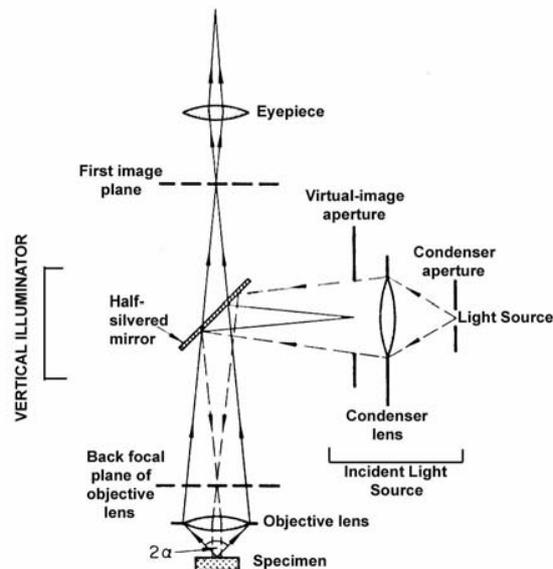
Fig.l. Image formation in a metallurgical microscope employing bright-field illumination

The conventional form of illumination by which metallographic specimens are illuminated for microscopic examination is known as bright-field illumination --a condition of lighting that renders a dark image on a bright, well-lit background field. Bright-field illumination is obtained by means of a vertical illuminator which is mounted in back of the microscope objective. Light from the light source is directed into the vertical illuminator. Deviation of the incident light beam from the vertical illuminator into the objective is most commonly achieved by a plane-glass reflector or a half-silvered mirror inclined at a 45° angle to the axis of the incoming light from the source. The incident light hits the glass plate and is specularly reflected down along the optical axis of the microscope into the objective.

The prepared specimen (polished or etched) is placed on the microscope stage, its surface perpendicular to the optical axis of the microscope. It is illuminated by the light which emerges from the objective lens and which has been focused so that the beam is approximately parallel to the optical axis of the microscope. Thus the light incident upon the specimen is virtually normal to the surface plane of the specimen. This form of illumination is called "vertical illumination"; the specimen and the light incident upon it are at right angles to one another.

Light incident upon the specimen is reflected back from the specimen surface. Any light that reflects back from specimen features which are approximately normal to the optical axis (i.e. features that are perpendicular to the incident light beam) will enter the objective, pass through the plane glass reflector, travel on to the eyepiece, and will form the bright portion of the image one sees. Any light that is reflected back from features inclined to the optical axis (i.e. features that are not perpendicular to the incident light beam) will be scattered and will not enter the objective. Such features will thereby appear dark in the image one sees. The final image of the specimen, formed by the eyepiece(s) of the microscope, is thus bright for all features normal to the optical axis and dark for inclined features. In this way, the various microstructural features of a metallographic specimen --such as grain boundaries that have been etched to produce grooves with inclined edges, precipitate particles, and non-metallic inclusions --are all revealed in the image of the specimen. Figure 2 presents a schematic diagram showing bright and dark image areas corresponding to reflection from normal or inclined features on the specimen surface.
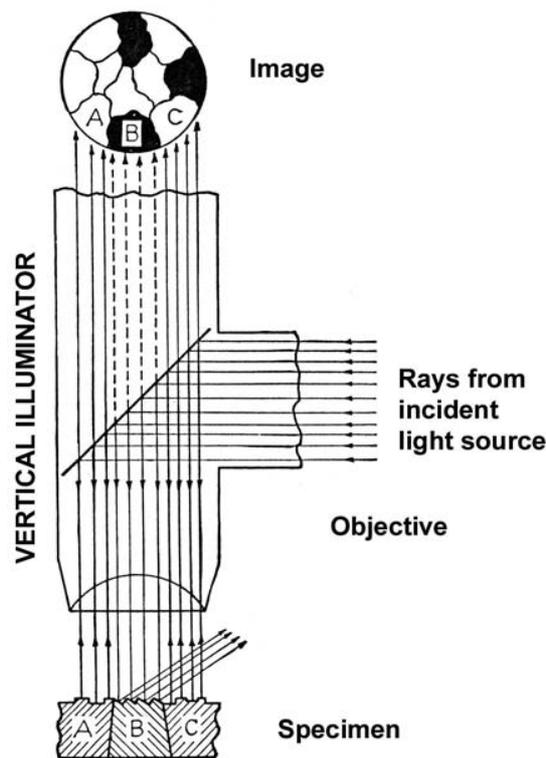
Fig.2. Specimen image under bright-field illumination.

Adjustable iris diaphragms

In the optical system of all metallographs (metallurgical microscopes with photographic attachments), there are appropriately placed two adjustable iris diaphragms --the aperture diaphragm and the field-of-view diaphragm. Figure 3 shows the relative placement of these two diaphragms on a specific metallurgical microscope. Their exact placement differs on various instruments.
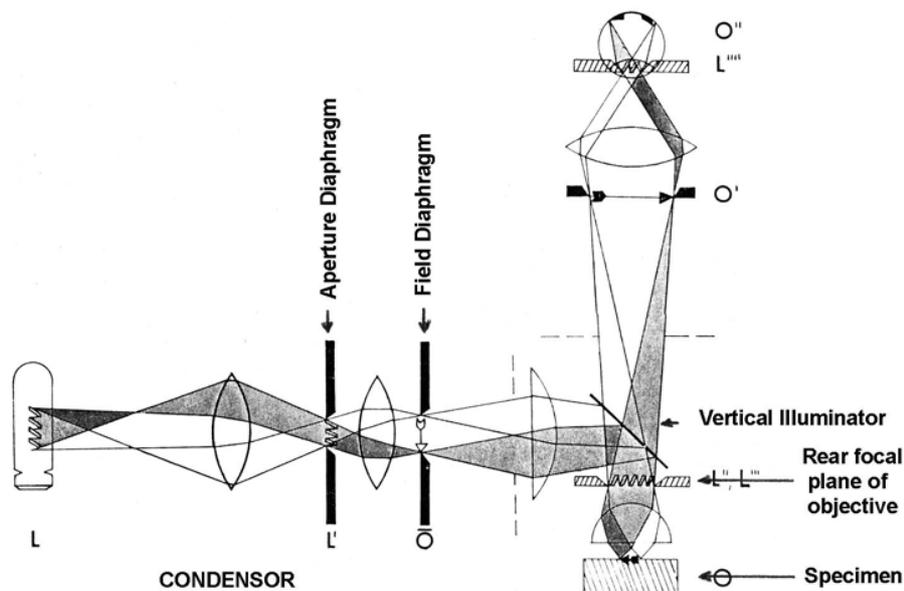
Fig.3. Position and function of the iris diaphragms

A. The aperature diaphragm

Regardless of its physical location, the aperture diaphragm is always positioned in the optical system so that by means of an interposed positive lens system, the diaphragm opening is imaged in the rear focal plane of the objective. Owing to this feature, it is generally possible to control the amount of light entering the objective by merely regulating the aperture diaphragm opening. Yet the aperture diaphragm must never be used to regulate the brightness of the image. It is used to regulate resolution, contrast, and depth of field.

The amount of light from the vertical illuminator that enters the rear lens of the objective, as governed by the opening of the aperture diaphragm, is of considerable importance with regard to the final quality of the image. The most important function of the aperture diaphragm is to increase the resolving power of the objective, i.e. its ability to render two closely spaced features of the sample as discrete images. As the aperture

diaphragm is stopped down, a point is reached at which the resolution of the objective is severely impaired, and the quality of the image is poor owing to the presence of pronounced interference fringes that surround features of the image. On the other hand, when the aperture diaphragm is completely open, internal glare and reflections within the microscope system become serious and impair image quality.

For any objective, there will be some optimum opening of the aperture diaphragm that will yield the best image. A good rule of thumb is to stop down the aperture diaphragm until all glare has been eliminated and the image just begins to darken but does not exhibit either surface topography or diffraction fringes. At this point, open the diaphragm just slightly, and leave it at that setting. The aperture diaphragm must be adjusted with each change of objective. The setting of the aperture diaphragm is crucial to good photomicrography.

Stopping down the aperture diaphragm will also increase the depth of field of the objective, i.e. the amount of vertical displacement of features on a specimen that can be tolerated without loss of focus. In most metallographic work, the goal is to observe a perfectly flat specimen and to avoid surface topography, that is, to avoid stopping down the aperture diaphragm to the point at which topography begins to appear or to become exaggerated. Stopping down the aperture diaphragm to the point at which the image begins to exhibit depth should be avoided. It should also be kept in mind that the resolving power of the objective is reduced as the depth of field is increased.

Finally, the aperture diaphragm can be used to regulate image contrast. As the diaphragm is stopped down, image contrast increases. The optimal setting of the aperture diaphragm is one at which the resolving power is at a maximum and contrast is sufficient to bring out features that are otherwise difficult to distinguish from their surroundings.

B. The field-of-view diaphragm

The principal function of the field-of-view diaphragm is to minimize the internal glare and multiple light reflections within the microscope system which, when achieved, markedly improves contrast in the image.

The diaphragm is so positioned that an image of the diaphragm opening is projected into the plane of the specimen surface, thus rendering the edge of the diaphragm visible in the image field when the microscope is focused.

When the field diaphragm is stopped down, the size of the image field is reduced, but at a gain in image contrast owing essentially to elimination of internal light flare within the microscope. Neither resolution nor image brightness is affected by the aperture of the field diaphragm.

To contribute to good image quality in visual examination, the field diaphragm should be stopped down until the image of the diaphragm leaves just begins to enter the field of view. At this point, open the diaphragm just slightly so that the leaves are no longer visible.

Dark-field illumination

A method that often is used to distinguish features <u>not</u> in the plane of the polished and etched surface of a metallographic specimen is dark-field illumination. This type of illumination gives contrast completely reversed from that obtained with bright-field illumination -- the features that are light in bright-field will be dark in dark-field, and those that are dark in bright-field will be light in dark-field. This highlighting of angled surfaces (namely, those of pits or cracks) allows more positive identification of their nature than can be derived from a black image under bright-field illumination. Generally, the same resolution can be obtained by the two techniques, but often features that have poor contrast in bright-field will have considerably increased contrast in dark-field.

The principles of dark-field illumination are illustrated in Figure 4.
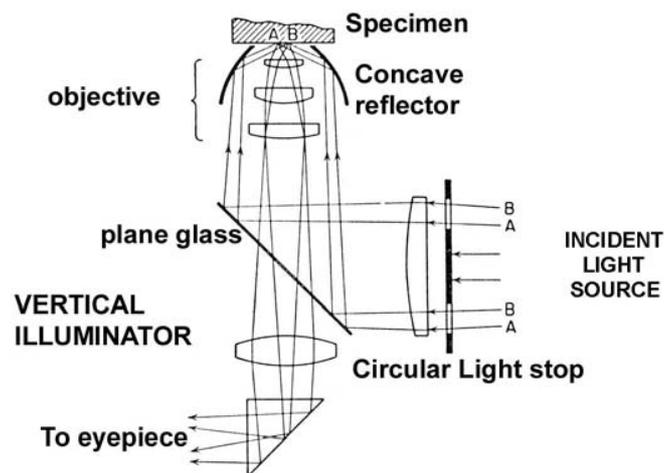
Fig.4. Dark-field illumination in an inverted stage microscope

By means of a circular stop appropriately interposed in the path of the incident light beam, the illumination enters the vertical illuminator in the form of a hollow cylinder or cone of light. The incident light reflected from the plane-glass reflector is then passed along the <u>outside</u> of the microscope objective and is reflected onto the specimen surface by a concave metal reflector. Because of the light stop blocking out the central portion of the illuminating beam, no light whatsoever passes into the objective.

The light incident upon the surface of the specimen is incident at a highly oblique angle. Thus the flat areas of the specimen --those that are normal to the optical axis of the microscope --will reflect such light so as to scatter it out of the path of the objective. Since no light will enter the objective from such areas, they will appear dark in the image. Portions of the specimen surface, such as etched grain boundaries, that are inclined with respect to the optical axis, may reflect the oblique incident light into the path of the objective. When that takes place, such inclined features will appear bright in the image. Thus the image rendered by dark-field illumination will be complementary, with respect to light and dark areas, to that obtained by bright-field illumination.

Polarized-light microscopy

Because many metals, mineral corrosion products, and metallic and non-metallic phases are optically anisotropic, polarized light is particularly useful in metallography. The principles behind polarized light metallurgical microscopy are presented in Figure 5.
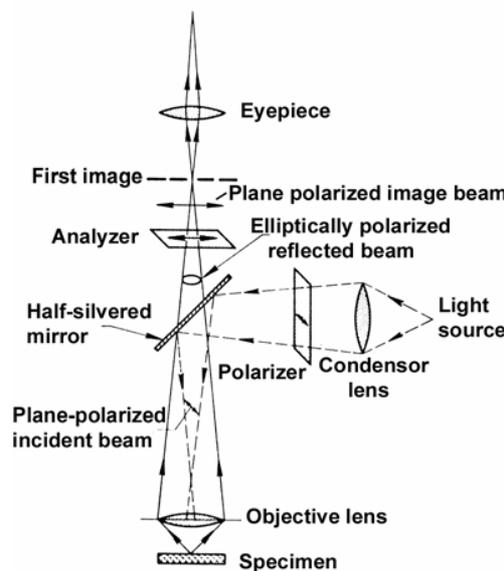
Fig.5. Basic components of a polarizing light microscope

Polarized light is obtained by placing a polarizer in front of the condenser lens of the microscope and placing an analyzer behind the eyepiece, as illustrated in Figure 5. Using this arrangement, the specimen is illuminated by plane-polarized light. When this light is reflected from an isotropic surface it remains plane polarized and remains completely extinguished when the analyzer is rotated. On the other hand, the light that is reflected from an anisotropic surface has a component that is perpendicular to the plane of polarization of the incident light, therefore the image does not remain extinguished when the analyzer is rotated, but changes alternately from dark to light with every 90^0 of rotation. This occurs because the optical properties of anisotropic materials vary with crystallographic direction.

Polarized light is particularly useful in metallography for revealing grain structure and twinning in anisotropic metals and alloys and for identifying anisotropic phases and inclusions. Polarized light has also been used for direct observation of phase transformations in alloys in which one or more of the phases is anisotropic.

FORMAT FOR NOTES ON THE EXAMINATION OF METAL OBJECTS

Object #: _____
Date of Examination:_____
Name of examiner:_____

OBJECT: Title or other functional description

PROVENANCE: Excavation site; Museum designation and catalogue
                                 number if available; private collection, etc.

DRAWINGS: Usually three views (front, back, side) with appropriate
                                 dimensions, in metric system.

GENERAL DESCRIPTION: Probable function of object; weight; appearance; use-
                                 wear; tool marks; adhesions (textiles etc.) and surface
                                 description; detail diagrams should be used wherever
                                 necessary to explain text.

CONDITION: Damages; repairs; any evidence of previous conservation;
                                 state of corrosion, corrosion products, metallic state;
                                 accretions.

METHOD OF
MANUFACTURE: Casting or worked metal; evidence of working; evidence
                                 of joining; evidence of the use of molds (e.g. flash lines
                                 etc.); pouring sprues; evidence of ceramic cores, chaplets
                                 etc.; detail diagrams should be used as much as possible
                                 to explain text.

SAMPLES
REMOVED: Description and diagram indicating location of any
                                 sample taken of corrosion products, textile or
                                 accretionary material, metal etc.; description of sampling
                                 procedure; numbering of all samples.

METALLOGRAPHY :   Description of sample and clear diagram of location of
                                 sample on object; description of mounting procedure,
                                 sample orientation, sample preparation, etchants used,
                                 analysis of metallic structures.

REFERENCES TO   Notebook references to X-ray diffraction,
ANALYTICAL WORK: X-ray fluorescence, chemical analyses, spectrographic
                                 analyses, X-radiographs, etc.

PHOTOGRAPHIC RECORD:

Example of Artifact Drawing: Axe

FACE A

LENGTH 15.4 cm
MAX THROUGH MIDSECTION

4.72 cm

1.08 cm

0.5 cm THROUGH MIDSECTION

FACE B

Example of Artifact Sample Drawing:Axe

FACE A

FACE OF SAMPLE
MOUNTED

SAMPLE 3303-A

3303-A-4

A   B

3303-   3303-
A-2   A-3

3303-A-1

FIGURE 14

A   B

3303-A-13 →   3303-
              A-14   ← 3303-A-15

3303- A-12
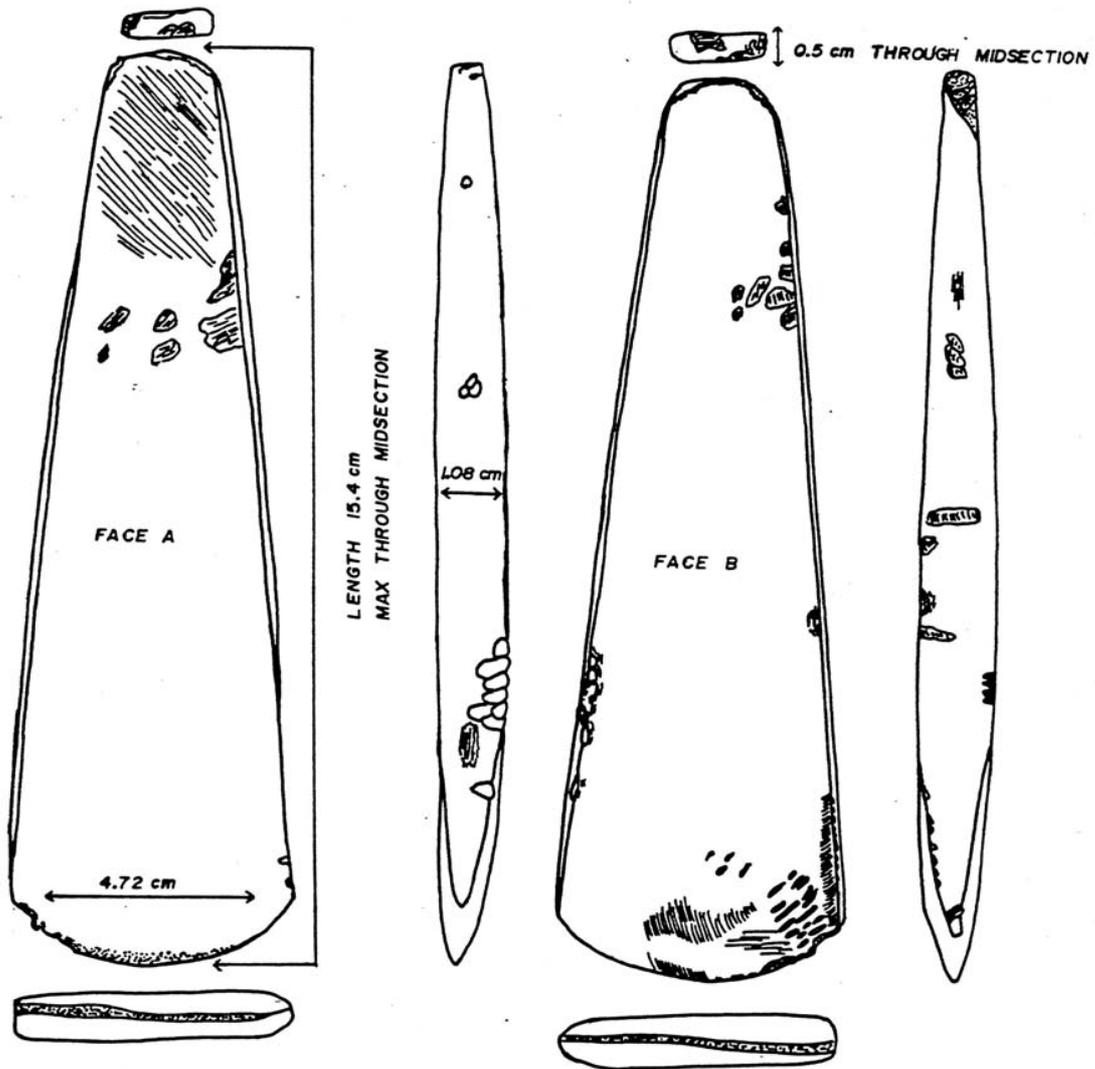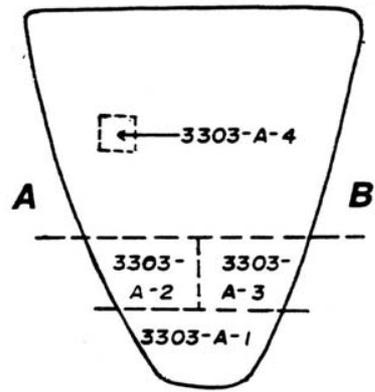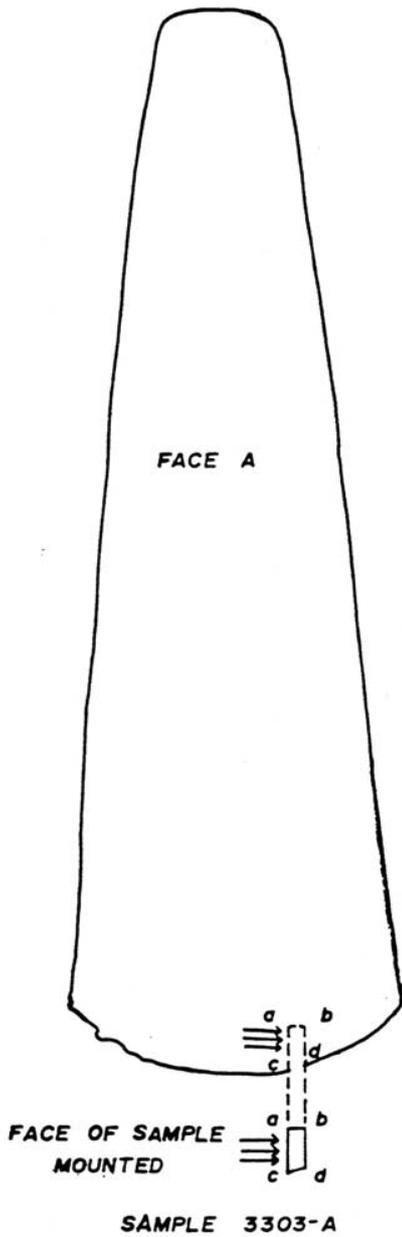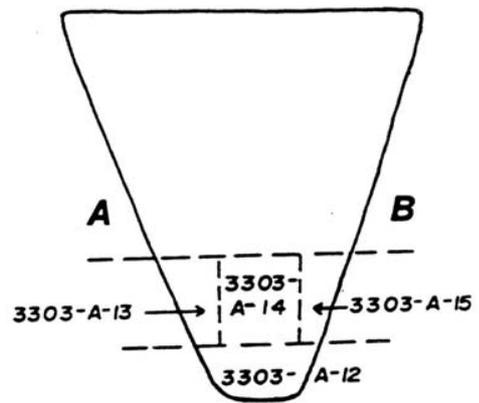
Example of Artifact Sample Drawing: Needle
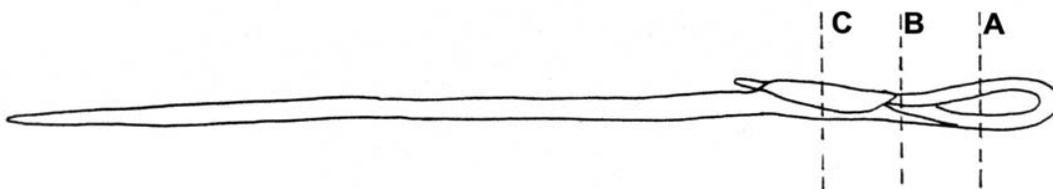
SECTION A

SECTION B

SECTION C
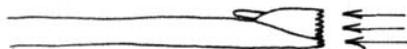
Example of Artifact Drawing: Nose Ring

27.7 mm

25.1 mm

3.5 mm

SIDE A

3.5 mm

5.1 mm

5.0 mm

2.3 mm

28.1 mm

9.45 mm

9.7 mm

3.5 mm

4.0 mm

5.2 mm

2.05 mm

6.1 mm

37.7 mm
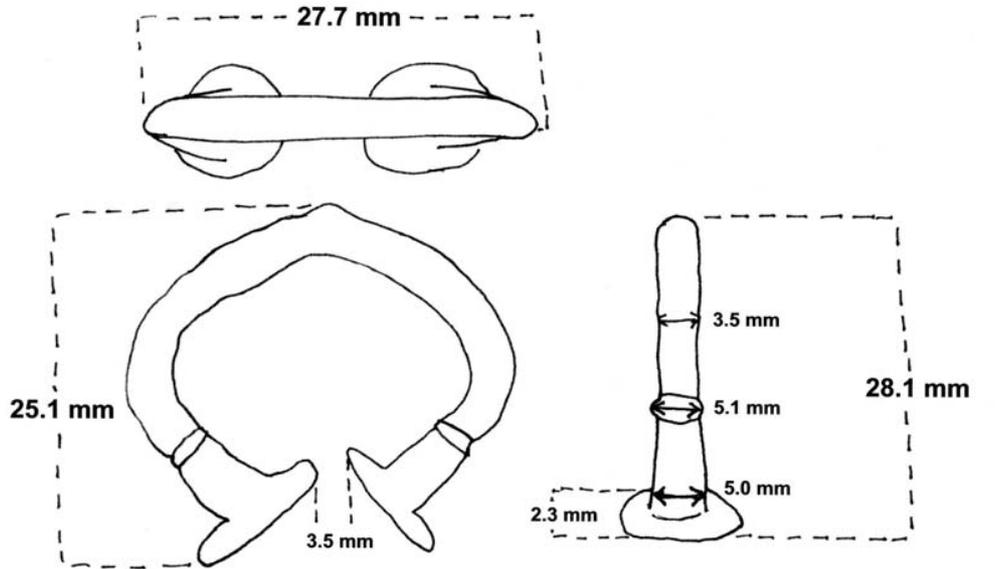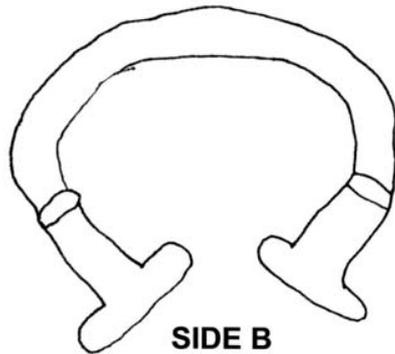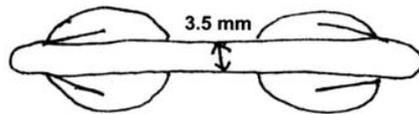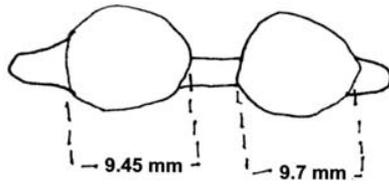
SIDE B
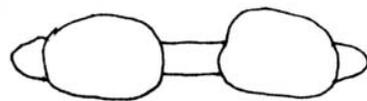
Example of Artifact Sample Drawing: Nose Ring
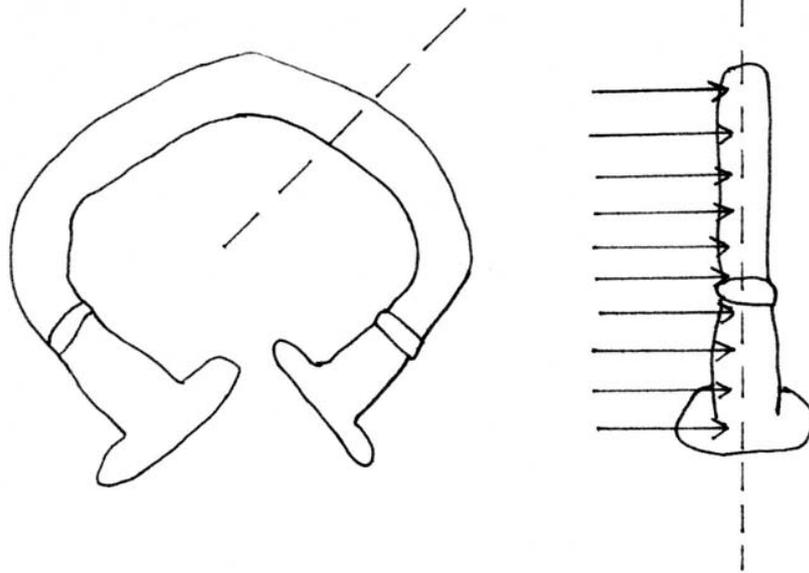
RECORDING THE RESULTS OF METALLOGRAPHIC EXAMINATION

The visual evidence of the microstructures observed should be described, preferably with accompanying photographic records of the microstructure at suitable magnifications. Inclusions or corrosion products which are present when the section is examined in the polished condition should be noted, because these will either be dissolved or partially obliterated by etching. If necessary, a photograph should be taken in the unetched condition to show the range and type of inclusions present. Examine them also in reflected polarized light which may assist in identifying the range and composition of non-metallic material.

It is important to obtain an overall view of the specimen at a low magnification first (about 30x -50x) before proceeding to look at particular features at higher magnifications (l00x –l000x). Some specimens will appear almost featureless before etching if the metal or alloy is uncorroded and relatively free from slag particles, oxide inclusions, or other impurities. In these cases one may proceed to an etched surface quite early in the examination. The details of the etching solution used should be recorded; it is not customary, however, to quote the time of immersion in the etchant, because the conditions of use and strength of solutions vary from laboratory to laboratory, making exact comparisons difficult. The magnification should be recorded with any notes made about the structure or with any photographs taken of it.

The range of features which may be made visible by etching is quite variable, depending on the type of specimen examined; detail not apparent using one etchant may become visible only after another reagent has been tried. Often all the microstructural detail will become evident only through the use of several etchants, one after the other.

The following are the kinds of features to be noted:

1. The sizes, shapes, and types of grains present.

2. The presence and distribution of different phases.

3. Gross chemical or other heterogeneity or differences in structure between various areas of the sample.

4. Cutting edges and worked surfaces: heat-treated zones, grain sizes, surface deformation, heat-treated zones.

5. The distribution of inclusions, fissures, slag particles, or porosity.

6. The presence of any surface coating or gilding.

7. The distribution of any corrosion products present and the existence within corrosion layers of: pseudomorphic remnants of grain structure or other microstructural features; the presence of any remnant metallic grains; layering or unusual features present within the corrosion products.

8. Indications of grain boundary thickening or precipitation of another phase at the grain boundaries.

9. The presence of twins within the grains and whether the twins are straight or curved; are they annealing twins or mechanical twins.

10. The presence of strain lines (or slip lines, as they may also be called) within the grains.

11. Whether dendrites, in cast alloys, show indications of coring.

12. The presence of intercrystalline or transcrystalline cracking in the specimen.

13. Indications of grain boundary thickening.

14. The presence of second phase precipitation at the grain boundaries (discontinuous precipitation) or precipitation within the grains (as in the case of Widmanstätten precipitation).

15. Evidence of martensitic transformations or heat treatment used in the fabrication process.

16. Do not forget that a polished section is a two-dimensional representation of a three-dimensional object. In some cases, such as with ancient wire, both a transverse and longitudinal section will greatly assist in interpretation of the method of fabrication.

There may be, of course, other important structural details but this brief list covers most of the features which may be visible using the metallographic microscope.

SOLIDIFICATION IN EUTECTIC SYSTEMS

The copper-silver alloy system will be used as an example of solidification in eutectic systems.
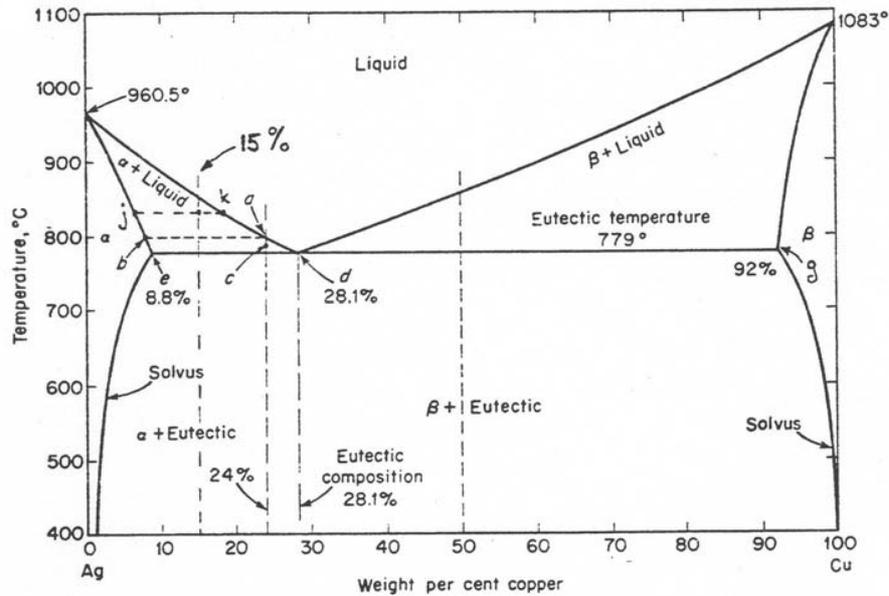
1. Silver will hold up to 8.8% copper in solid solution. Thus any Ag-Cu alloy which lies within the composition range of 0 -8.8% Cu, when molten, will solidify with the formation of crystals of a solid solution. The composition of the α solid will be the same as that of the original liquid from which it forms (though the a grains may be cored). Thus α grains may range in composition from close to 100% Ag to 91.2% Ag/8.8% Cu, depending upon the composition of the liquid. Alpha grains are always single phase.

The same process takes place at the copper-rich side of the constitution diagram. Copper will hold up to 8% silver in solid solution. Any Ag-Cu alloy which lies within the composition range of 0-8% Ag, when molten, will solidify with the formation of β solid solution. These β grains will range in composition from almost 100% Cu to 92% Cu/8% Ag, depending upon the composition of the origina11iquid. The solid solution that forms has the same composition as the liquid from which it formed, and all β grains are single phase.

2. Silver can hold no more than 8.8% Cu in solid solution. It is essentially saturated with copper at that composition, and its matrix cannot accommodate more copper atoms. Similarly, copper is saturated with silver at the concentration level of 8% silver. No more silver atoms can be held by the copper matrix.

For alloys between the composition range of 91.2% Ag/8.8% Cu and 92% Cu/8% Ag another mechanism operates during solidification to handle the liquid that is beyond the limits of the two solid solution fields.

3. Consider an alloy of 15% Cu, 85% Ag. It will begin to freeze at about 850°C (where the vertical line representing that alloy intersects the liquidus curve). Small nuclei of α solid solution will form in the α + Liquid field (note that this is a 2-phase field). As the temperature of the alloy drops, these primary a crystals will grow as more liquid freezes. At any temperature, the compositions of the growing α grains and of the remaining liquid are given by the intersections of a horizontal tie line, drawn at that temperature, with the solidus and liquidus curves.

For example, at about 830°C, the composition of the primary α grains growing in the liquid is given by point j: 6% Cu in 94% Ag. The composition of the remaining liquid at this temperature is given by point k: 18% Cu in 82% Ag.

4. As the temperature continues to drop, the primary α grains continue to grow and less and less liquid remains. At 800°C the composition of the primary α grains is given by point b: 8% Cu, 92% Ag. The composition of the remaining liquid is given by point a: 25% Cu, 76% Ag.

5. When the temperature drops further and reaches 779°C, the primary α grains have reached the saturation concentration of copper in silver, given by point e: 8.8% Cu in 91.2% Ag. The remaining liquid has reached the composition of the eutectic alloy, given by point d: 28.1% Cu in 71.9% Ag. At this temperature the primary α crystals have grown as large as they can; no more a crystals can form. All of the remaining liquid freezes through the eutectic transformation. When the primary α crystals have grown dendritica11y, the eutectic solid or eutectic microconstituent will fill in the spaces between α dendrite arms to complete the solid grain.

6. Referring to the Ag-Cu constitution diagram, all alloys below 779°C will be solid. This temperature is known as the eutectic temperature and represents the lowest freezing point of any alloy in the entire system.

All solid to the left of the eutectic composition will be composed of primary α phase surrounded by eutectic microconstituent; all solid to the right of the eutectic composition will be composed of primary β phase surrounded by eutectic microconstituent. Note, however, that the eutectic microconstituent is identical in composition no matter whether it has formed from eutectic alloy (alloy of eutectic composition), from liquid in the α + Liquid field or from liquid in the β + Liquid field. The eutectic microconstituent always forms from liquid that has arrived at the eutectic composition, in this case 28.1% Cu 71.9% Ag. When it freezes it will always form the same eutectic solid.

7. The eutectic solid is a two-phase solid composed of a finely divided mixture of small grains of the α solid solution and the β solid solution. If one considers liquid that has reached the eutectic composition and is at the eutectic temperature, a tie line (known as the eutectic horizontal) drawn through this point will intersect the α and β solid solutions.

Thus the eutectic liquid freezes to form solid composed of α and β phases that are in intimate association.

Phase	Composition
α solid solution	8.8% Cu, 91.2% Ag
eutectic liquid	28.1% Cu, 71.9% Ag
β solid solution	92% Cu, 8% Ag

Since the α solid solution needs more Ag than the liquid contains in order to form; since the β solid solution needs more Cu than the liquid contains in order to form, the two solid solutions form contiguously in the liquid, each solid giving up to the other the component it has to lose and obtaining from the other the component it has to gain. This sharing occurs by solid state diffusion of silver and copper atoms across the common boundary between adjacent solid phases.

8. Within that portion of the phase diagram where the eutectic transformation occurs, the primary α or primary β crystals never change their composition, i.e. they are always at the saturation composition of the α and β solid solutions. It does not matter what the composition of the original molten alloy is.

      The composition of the molten alloy determines:
      a) Whether primary α crystals will form or whether primary β crystals will form during solidification.
      b) The proportion of primary α (or primary β) and of eutectic microconstituent in the final solid (i.e. the ratio of α to eutectic or the volume fraction of one with respect to the other).

9. The lever law is a convenient way to predict the amount of any phase that will be present upon solidification of a given alloy. Consider the following diagram which represents part of an equilibrium phase diagram showing a liquid region, a solid region, and a 2-phase liquid + solid region.
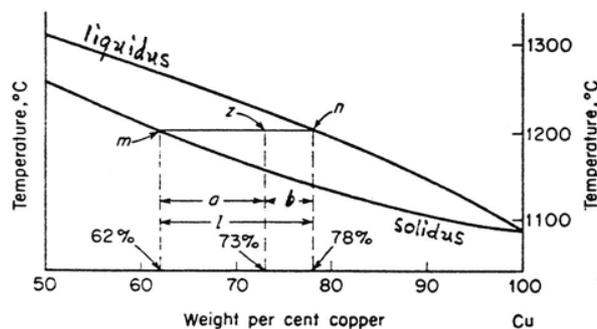
The lever rule.

      Given a point such as z which lies inside a two-phase region:
      a) Find the composition of the two phases. Draw a tie line through z. The intersections of the tie line with the boundaries of the 2-phase region (points m and n) determine the composition of the phases.

b) Find the relative amounts of the two phases. Determine the three distances a, b, and 1 (in units of percent composition). The amount of the phase corresponding to point m (here, the solid) is given by the ratio b/l, while that corresponding to point n (here, the liquid) is given by a/l .

10. Let us apply the lever rule to three different alloys in the Ag-Cu diagram.

1) The 15% alloy (i.e. 15% Cu, 85% Ag)
Determine the relative amounts of primary alpha of the eutectic microconstituent when all the liquid has solidified.

m = 91.2% Ag	a = 91.2 -85 = 6.2
n = 71.9% Ag	b = 85 -71.9 = 13.1
z = 85% Ag	l = 91.2 -71.9 = 19.3

amount of α = 13.1/19.3 = 67.8%

the remaining portion of the solid must be eutectic: 100 -67.8 = 32.2% or amount of eutectic = 6.2/19.3 = 32.1%

2) The 24% alloy (i.e. 24% Cu, 76% Ag)
Determine the relative amounts of primary alpha and of the eutectic microconstituent when all the liquid has solidified.

m = 91.2% Ag	a = 91.2 -76 = 15.2
n = 71.9% Ag	b = 76 -71.9 = 4.1
z = 76% Ag	l = 91.2 -71.9 = 19.3

amount of α = 4.1/19.3 = 21.3%

N.B. The amount of α is considerably less than for the 15% alloy, as would be expected, since the α grains solidify through a small drop in temperature and do not have much chance to grow.
The remaining portion of the solid must be eutectic: 100 -21.3 = 78.7%

3) The eutectic alloy (i.e. 28.1% Cu, 71.9% Ag)
This time, we are in a 2-phase field in which both phases are solid: the α phase and the β phase which, together, form the eutectic microconstituent. Determine the relative amounts of α and β in the eutectic:

For α:		
	m = 91.2 (100-8.8)	a = 91.2-71.9 = 19.3
	n = 8.0	b = 71.9 – 8 = 63.9
	z = 71.9 (100-28.1)	l = 91.2 – 8 = 83.2

amount of α = 63.9/83.2 = 76.8%
The remainder must be β: 100 – 76.8 = 23.2%
Or β = 19.3/83.2 = 23.2%

The ratio of α to β in the eutectic microconstituent formed upon solidification of the 15% and the 24% alloys will be exactly the same as their ratio in example #3. There will be less eutectic formed in examples #1 and #2, but within the eutectic, the ratio of α to β is constant.

POINT COUNTING

Reference: E. E. Underwood, <u>Quantitative Stereology</u>, Addison-Wesley, 1970.

Point counting is one of the simplest operations of quantitative stereology. The term refers to test points (for example, the intersections of an orthogonal test grid) that are counted when they superimpose on some areal feature of interest in the microstructure of a metallographic cross section. Such features may be individual phases, pores, or inclusions present in the structure. The point counting technique allows determination of the volume fraction of such features in the specimen under study.

When a metallurgical microscope is used for point counting, one can use a special reticle in one eyepiece which provides an orthogonal grid whose intersections constitute the test points. One can also use the single intersecting point of the cross hairs in one eyepiece which, together with the systematic movement of the mechanical stage, provides an orthogonal grid of test points. Or one can superimpose a grid on a photomicrograph.

The ability to count systematically the occurrence of a feature within a given area on a plane surface and to translate that count into the volume fraction of that feature within the material under study is based on the following relation:

$$\frac{\text{The number of points P that fall on feature F}}{\text{The total number of points counted}} = \frac{P_F}{P_T} \text{ (point fraction)}$$

is equal to:

$$\frac{\text{The volume feature F}}{\text{The total volume of the sample}} = \frac{V_F}{V_T} \text{ (volume fraction)}$$

In any given area of the specimen, one counts the number of grid points that fall on the feature of interest (e.g. a given phase or a type of inclusion). The sample is moved so that another representative area can be examined, and the counting is continued until a statistically significant number of measurements has been made. The total number of points falling over the feature of interest divided by the total number of points in the grid (P_F/P_T) gives the volume fraction of the feature in the specimen.

It is important that the areas over which counting takes place be representative and chosen at random. Systematic exclusion or inclusion of features in the microstructure destroys the point fraction-volume fraction relationship.

Point counting with the Metallurgical Microscope

1. Random-walk method

    a. Place the polished and/or etched section on the stage and adjust the magnification so that the feature of interest is easily seen. Select, at random, a representative portion of the sample.

    b. Using a reticle with a cross hair in one of the eyepieces, begin counting by observing the nature of the material beneath the cross hair, i.e., does the cross hair fall on a feature of interest or on the rest of the material. A count is recorded for the feature if it lies under the cross hair. If not, the test point is recorded.

    c. Move the stage by a small motion, randomly, in any direction, thereby moving the specimen under the cross hair. Observe the nature of the material under the cross hair. A count is recorded for the feature; a test point is recorded for the rest of the material.

    d. This procedure is repeated until a statistically significant number of points has been counted (see Underwood). Dividing the number of counts for the feature by the total number of points tested gives the point fraction of the feature or its volume fraction in the specimen.

2. Systematic method

    a. Place the polished and/or etched section on the stage and adjust the magnification so that the feature of interest is easily seen. Select, at random, a representative portion of the sample.

    b. If a reticle is available with an orthogonal grid, this is placed in one of the eyepieces. Counting is accomplished by recording the identity of the material over which each grid point lies, i.e., a count is made of all points on the grid that lie over the feature of interest. The point fraction of that feature is its point count divided by the total number of test points on the grid.

    c. Move the stage so that another area of the specimen is in view and repeat the process. Continue the procedure in discrete areas of the sample until good counting statistics have been achieved.

        N.B. The choice of grid size and microscope magnification are important. They must be chosen so that only one point of the grid falls on a feature of interest.

    d. If a reticle with an orthogonal grid is not available, a reticle with a cross hair can be used instead. An "imaginary" orthogonal grid can be realized by moving the mechanical stage by predetermined and fixed increments first in one direction

and then in the orthogonal direction. A count is made of the material under the cross hair each time the mechanical stage is moved.

Sweeping out a rectangular grid
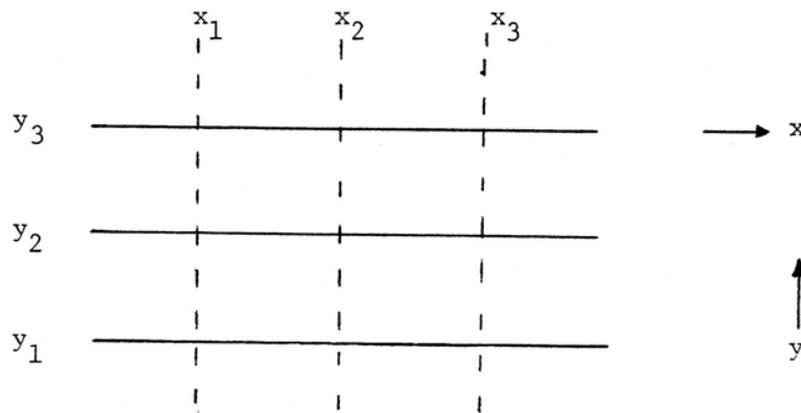
(1) Set the stage at position y_1 and count under the cross hair, moving the stage from x_1 to x_2 to x_3 …

(2) Reset the stage to position x_1 and move the stage to position y_2. Count from x_1 to x_2 to x_3…

(3) Repeat the operation to provide statistically reliable data.

(4) Note that the increments along the x axis need not be the same as the increments along the y axis, as long as all increments along anyone axis are kept constant.

Point Counting with a Photomicrograph

1. One or several photomicrographs of the section being studied should be taken at appropriate magnifications to reveal the desired features. The field of view for such micrographs must be chosen at random.

2. Superimpose a grid of suitable spacings on the photomicrograph. The grid size is chosen so that only one test point will fall on a feature of interest.

3. Count the number of grid points that fall on a feature of interest. The point fraction is simply the number of points falling on features of interest divided by the total number of test points on the grid.

4. The grid may be moved to another area of the photomicrograph in a systematic or a random fashion and counting resumed.

DETERMINATION OF ALLOY COMPOSITION THROUGH POINT COUNTING OF METAL PHASES

Eutectic Solidification in a Binary Alloy: The Cu-Ag System

Consider a binary alloy such as Cu-Ag which, beyond the solid solubility limits, solidifies as a two phase solid of primary alpha phase plus eutectic or primary beta phase plus eutectic.

Point counting the phases present in a polished and etched cross section of the solid will yield the volume fraction (% volume) of the alpha phase and of the beta phase in the solid. The alpha and beta phases are present in two forms: as primary crystals, and as part of the eutectic microconstituent. Both occurrences must be included in the point count for each phase.

In order to determine the composition of the solid and of the original molten alloy, i.e., the weight percents of copper and silver present, we need to determine the weight fraction (weight %) of each phase in the solid, using the relation among density, weight, and volume:

$$\delta_{phase} = (W_{phase} / V_{phase})$$

and $W = \delta V$

where W = wgt. fraction of the phase
        V = vol. fraction of the phase
        δ = density of the phase

Determination of V (volume fraction of each phase): The value of V for each phase is given by the point count of each phase.

Determination of δ (density of each phase): Each phase is a solid solution composed of two elements, Cu and Ag. The density of the phase is given by

$$\delta_{phase} = [\text{wgt. \% Cu in the phase x } \delta_{Cu}] + [\text{wgt. \% Ag in the phase x } \delta_{Ag}]$$

The densities of the elements Cu and Ag are known:

$\delta_{Cu} = 8.92$ grams/cc $\delta_{Ag} = 10.5$ grams/cc

It remains, therefore, to obtain the weight percent of Cu and of Ag in each phase, i.e., the composition of each phase.
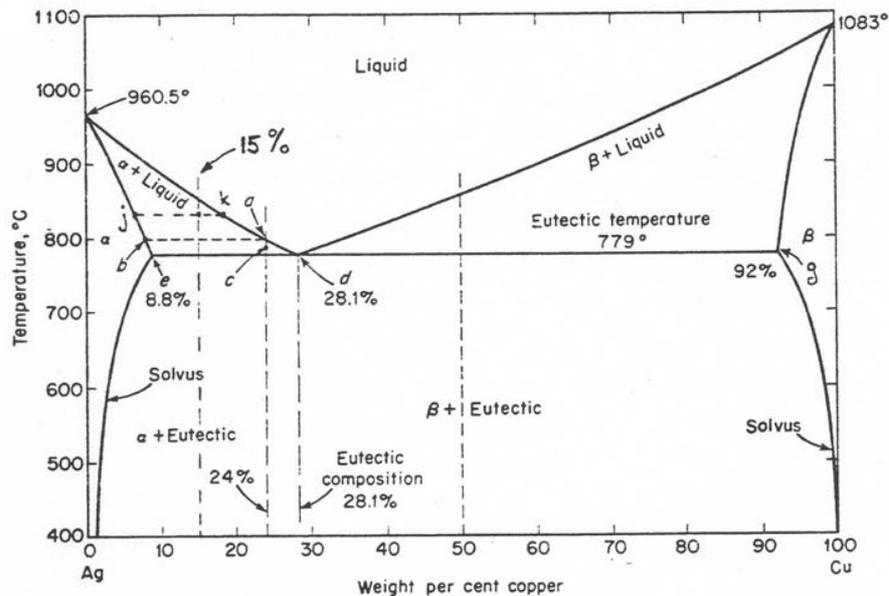
Referring to the Cu-Ag constitution diagram, we see that below the eutectic temperature both the alpha and the beta phase have decreasing solubilities with decreasing temperature. Since the conditions under which the alloy cooled are unknown, the composition of the alpha phase is also unknown and can be anywhere between 8.8% Cu in Ag and 2% Cu in silver. Similarly the composition of the beta phase can be anywhere between 8% Ag in Cu and 0% Ag in Cu. The composition of each phase can be:

> (1) measured, with an electron microbeam probe or with a scanning electron microscope in an analytical mode. Both will furnish values of weight percent Cu and Ag in each phase. If the composition of only one phase is measured, the temperature corresponding to that composition can be determined from the constitution diagram, and the composition of the other phase can be determined directly from the diagram at that temperature.

> (2) chosen from the constitution diagram. Since the conditions under which the alloy solidified are unknown, one has to choose a value of the solid solution achieved for each phase from between the maximum solid solubility it is possible to obtain and the minimum value realized under equilibrium conditions (slow cooling). A calculation of δ_{phase} for the situations of maximum and minimum solid solubility for the phase will indicate the spread in the value for δ and the magnitude of possible error involved when choosing a value for the solid solubility achieved. The choice may be no more than a good guess, but if the

analytical instruments are not available to measure the phase compositions, some judicious decision must be reached by referring to the phase diagram.

Determination of W (weight fraction of each phase):

$$W_{phase} = \delta_{phase} V_{phase}$$

Determination of the composition of the alloy

The composition of the alloy is given by the weight of each metal present. Let us assume, as an example, that the alpha phase contains 6% Cu and 94% Ag and constitutes 40% by weight of the solid (i.e., we have determined that its weight fraction is 40%). Assume that the beta phase contains 95% Cu and 5% Ag and constitutes 60% by weight of the solid.

The total weight of Cu in the solid is given by

wgt. Cu   =   (wgt. % Cu in α) (wgt. fraction α) +
[in grams]   (wgt. % Cu in β) (wgt. fractionβ)

or

wgt. Cu   =   0.06(0.4) + 0.95(0.6)
[in grams]   alpha   beta

The same calculation can be made for the weight of silver in the solid, or the weight of silver can be obtained by difference.

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