Spring 1940

Metallurgical Examinations in Criminal Cases

Gustav W. Pirk

METALLURGICAL EXAMINATIONS
IN CRIMINAL CASES

GUSTAV W. PIRK†

Pieces of metal frequently play an important part in the solution of a crime. At times a physical examination or a chemical analysis will suffice, but very often a study of the fine internal structure of the metal is also of considerable importance. Although in a given sample a chemical analysis will disclose the percentage of each element present, it tells nothing about the way these elements are combined or arranged within the specimen. It is the form, size, and arrangement of the various microstructural constituents which are of particular significance to the forensic metallurgist.

By way of illustration suppose that two pieces of ordinary brass are presented for laboratory examination to determine whether or not they are identical. The results of a physical examination and a chemical analysis reveal that they are similar in external form and appearance, and that both contain 70% copper and 30% zinc. The tendency at this point would be to declare the two pieces of metal identical. However, until a microscopic examination has been made the question of identity cannot be considered completely answered. Therefore, a sample is taken, polished, etched, and studied under the microscope. Observation is made of such features as the size and shape of the grains composing the sample, and

---

† Metallurgist, General Research Laboratories of the General Cable Corporation, Rome, New York; Consulting Metallurgist, Scientific Crime Detection Laboratory, Bureau of Police, Utica, New York.

also of such abnormalities as non-uniformity in grain size, impurities (which may be present as separate constituents), porosity, and mechanical defects (e.g., cracks of microscopic magnitude). Perhaps the microscopic examination may show that in one of the samples the grains are large, well-formed, uniform as to size and distribution, and equi-axed (i.e., have approximately the same dimensions in all directions); while in the other sample the grains are found to be elongated into fibres all running in the same direction, and are neither well-formed nor equi-axed. Obviously, then, these two samples of brass are different, because the arrangement of the grains which form their microstructure differ. If they were from the same piece of metal both would be similar in their micro-structural details. To the metallographer the well-formed grains which are uniform as to size, geometrical outline, and distribution, indicate soft or annealed brass; while on the other hand, the grains which are elongated into fibres indicate that the metal has been cold-worked, that is, it has had its shape altered by hammering, rolling, or drawing at room temperature—low compared to annealing temperatures (850° F. to 1000° F.), which would cause the well-formed grains observed in the first sample. (For a rather simple example of how grain structure characteristics may serve as the basis for a comparison between two pieces of metal see Figure 1.)

A   B
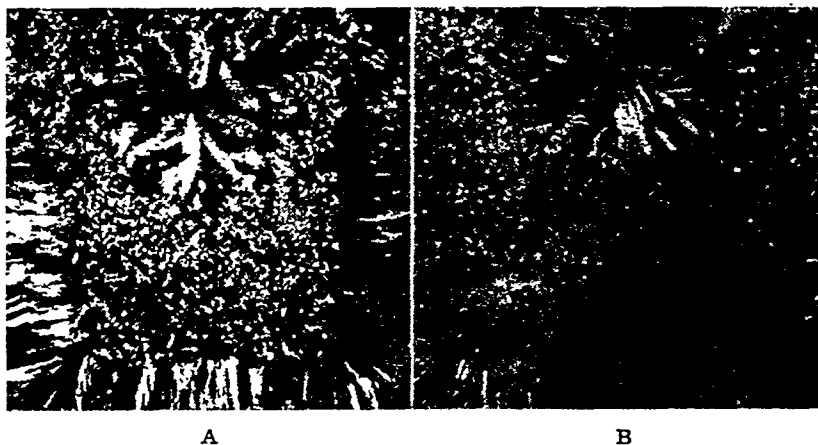
FIGURE 1

Cross sections of copper bars, illustrating the effects produced by different rates of cooling during the solidification process. In general, the more rapid the rate of cooling, the finer the grain sizes will become. In A observe the effect of rapid cooling of the center portion of the bar as compared with the moderately slow cooling rate of the outer portions. In B there was a rapid cooling of the center but a moderately rapid cooling of the surrounding area.

Microscopic examinations are especially valuable when the available pieces are small, for then the physical properties such as tensile strength, ductility, etc., cannot be determined. In addition, the tensile test is destructive, as it is necessary to pull the test piece apart in order to measure this property, whereas in a microscopic examination the sample is not destroyed but is carefully prepared and studied in its normal and unaltered condition. This statement, however, should not be interpreted as meaning that the tensile or other similar destructive tests have no place in criminal investigation; it merely is intended to indicate the greater advantages of a microscopic examination, especially when only a limited amount of material is available or when other tests prove inadequate.

Although this paper is primarily concerned with the microscopic examination of the constituents of metallic samples, it should be mentioned that the application of the spectograph is particularly well-suited to problems which involve the question of the probable identity of two or more specimens of metal. This method of comparison in most instances exceeds the sensitivity of chemical methods for qualitative analysis. Therefore, in the determination of small quantities of admixtures foreign to the principal components of the metal, a spectrographic analysis may be of assistance when other methods of comparison would fail. Another advantage of the spectrographic comparison is that extremely small metallic specimens will usually suffice for a qualitative comparison.[1]

Cases are on record in which the results of microscopic examinations of metals have been admitted as court evidence. Typical examples are the Magnuson case[2] and the Valier Coal Mine Bombing case.[3] Both cases illustrate very strikingly the effectiveness of a microscopic examination of metallic specimens as an incontrovertible form of evidence.

The preparation of the sample and the correct interpretation of the details which are observed in the subsequent microscopic

---

[1] Wilson, C. M., "Spectrographic Analysis as an Aid in Identification Problems," J. Crim. L. and Criminology, 25 (1): 160 (1934); Brode, W. R., Chemical Spectroscopy (1939); Miggers, W. F. and Scribner, B. F., "Index to the Literature on Spectrochemical Analysis 1920-37," Committee E-2 on Spectro. Analysis of the Amer. Soc. for Testing Materials (1939).

[2] Magnuson v. State, 187 Wis. 122, 203 N. W. 749 (1925).

[3] People v. McDonald, 365 Ill. 233, 6 N. E. (2d) 182 (1937). For a discussion of the laboratory techniques used in this case see Wilson, C. M., "The Comparison and Identification of Wire in a Coal Mine Bombing Case," J. Criminal L. and Crim. 28 (6): 873 (1938).

examination form very important and necessary steps before the results of the examination can be presented as court evidence. It is this phase of the problem which must now be considered.

A. SELECTING THE SAMPLE SPECIMEN

The metallographic sample, like any other sample, must be truly representative of the material which is being studied. If not, the most exacting polishing technique and the most expert microscopic examination will be wasted effort. In most instances the purpose of the examination will determine the location from which one or more specimens are to be cut. A few general rules, however, may be laid down which will aid in the proper selection of the sample.

In investigating the characteristics of a piece of metal, the examiner must be careful to collect an adequate number of samples. For instance, when studying a bar or strip of metal, or a piece of wire, sections should be taken not only from both ends but at several points between the ends, for even within the same piece of metal there will be some differences in grain structure. But, by taking a sufficient number of specimens from various parts of the metal object, its particular characteristics can be established.

Whenever two metal objects are to be examined with a view to determining whether or not they had been one piece originally, it is highly desirable, of course, to make the comparison examinations as near as possible to the fractured or cut ends.

Sometimes legal questions arise as to liability or responsibility for the cause of a failure in a metal part. In such cases the technician may be asked to determine whether or not the failure resulted from defects resident in the metal, from faulty design, or from some other cause. When such is the question at hand the specimen to be examined should be taken as close as possible to the point of fracture or initiation of failure. It is also advisable to obtain one or more specimens at a point in the sound part of the metal considerably removed from the failure in order to compare the structures of the sound and the defective portions. Comparisons of this kind generally yield valuable information. (Figure 2 is a typical example of the grain structure found at a point of fracture.)

Notches are of particular significance in diagnosing failures since they cause stress localization and consequently act as stress raisers, thus leading to what is known as a fatigue failure.[4] This is especially true where the parts involved are subjected to vibra-

---

[4] Fatigue failure is the phenomenon of progressive fracture of a metal by means of a crack which spreads under repeated cycles of stress.
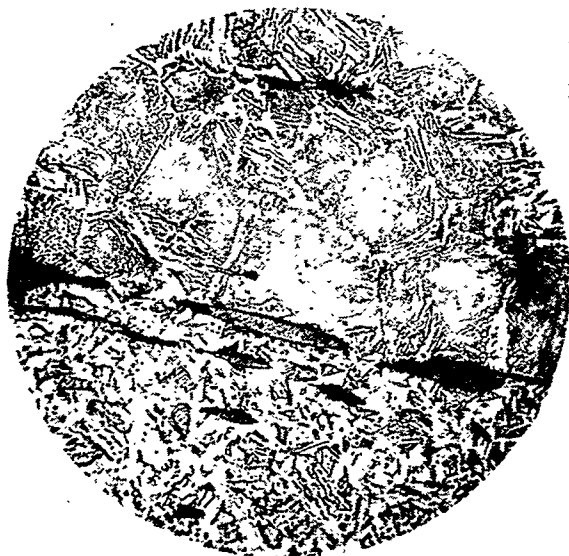
FIGURE 2

In the case in which the above illustration was used one of the parties contended that failure of the machine part was due to defective steel. The other party contended it was attributable to faulty design. The relatively large dark areas across the photomicrograph represent slag inclusions, possibly manganese sulphide; and the structural non-uniformity is indicative of segregation. The mechanism of the failure was probably something on the following order: the inclusions acted as notches and caused concentration of stress in these areas, resulting in the formation of a fatigue crack. (Note the crack at the left starting from one of these inclusions; and also observe the several cracks appearing at the right.) During operation of the machine the cracks gradually increased in size, reducing the. effective cross-section of the metal and thus increasing the stress on the remaining sound metal. When the cracks became sufficiently extensive so that the sound metal could no longer bear the load, it snapped suddenly. The accompanying structural non-uniformity referred to establishes the cause of failure.

tion or cyclic applications of a load. Sharp corners, tool marks and deep scratches can also act as stress raisers. In legal cases which involve the question of failure these should be looked for near the point of failure. For example, an insignificant looking scratch or nick may start a crack which will propagate itself under load, gradually weakening the structure through the reduction of the load-sustaining area until sudden and complete fracture finally occurs. Such a fatigue fracture has a characteristic appearance. A portion of the fractured surface appears silky or velvety, due to the polishing effects resulting from adjacent walls of the crack rubbing together during the period in which the crack has been propagating itself; while the remainder of the surface which failed suddenly after the remaining effective cross-sectional area was insufficient to carry the load appears as a bright, shiny, crystalline

surface. This phenomenon is somewhat inaccurately described by the popular expression "the metal crystallized," for in truth the metal was crystalline to begin with, and the failure is not due to the formation of crystals as might be inferred from this phrase, but to the breaking down or failure of the original crystalline aggregate.

In all cases, before destroying a fracture for metallographic examination it should be photographed and carefully examined for any typical or special features. For example, in tensile fracture, which is a fracture due to excessive tension, there will generally be a "necking down" or reduction of the cross-sectional area at the point of separation. Of course, microstructural defects, such as those already discussed, may be responsible for tensile failure at loads which the metal should normally sustain, and under such circumstances these defects should be carefully sought for.
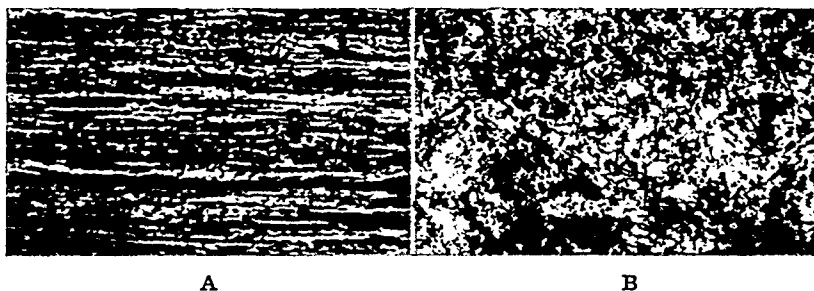

A   B

FIGURE 3

(A) Longitudinal section of a hard (drawn) copper wire. .049″ in diameter. Note how the grains have been elongated into thin fibres.

(B) Transverse section of same wire. Note the indefinite structure and the marked difference in appearance when compared with A.

Having decided upon the location of the particular sample, the type of section to be cut and examined must then be decided upon. The two most usual types of sections are transverse and longitudinal. A transverse section (i.e., one cut perpendicular to the outer surfaces), shows the variations in microstructure which exist from the outside to the center, while a longitudinal section (i.e., one cut parallel to the outer surface) shows the characteristics and variations found at a given distance below the surface. In either hot-worked or cold-worked metals both longitudinal and transverse sections should be examined. A study of Figure 3 will show the basis for recommending both types of sections in cold-worked products. The grain structures illustrated in this figure are from the same piece of hard-drawn copper wire. A longitudinal section (Fig. 3-A) shows the grains of copper elongated into fibres as a result of the normal wire-drawing process. This elongation of the

fibres indicates the direction of cold working (the direction in which the wire was drawn). A transverse section of the same piece of hard-drawn copper wire (Fig. 3-B) shows none of the directional indications present in the metal but rather only a cross-section through the many thin fibres present in the specimen. If a comparison is made of two pieces of cold-worked wire the probability of arriving at a dependable answer is much greater by a comparison of longitudinal sections than by comparison of transverse sections. (See Figure 4 for a comparison of longitudinal sections from two copper strips.)

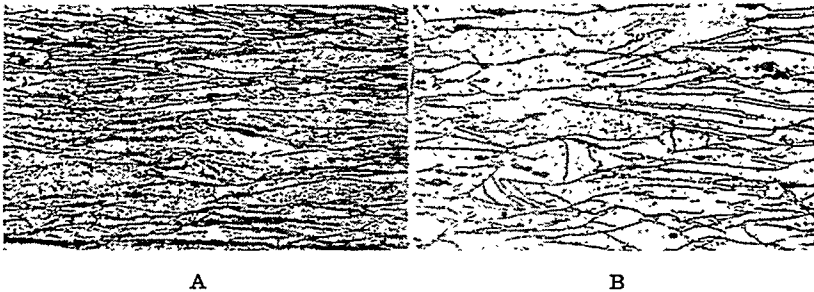A   B

FIGURE 4

Longitudinal sections of two copper strips. Although the cross-sectional areas of both specimens were reduced the same amount by the rolling process, the initial grain sizes differed, and this fact, which is apparent in the illustration, indicates conclusively that the two pieces are not of identical origin.

The information obtained from transverse sections can be summarized as follows: (1) Variation in structure from the center to the outside surface of the specimen; (2) Distribution and size of non-metallic impurities throughout the section, such as oxides, sulphides, etc.; (3) Surface alterations in general, such as decarburization[5] as the result of heating of ferrous material and the presence of sulphur penetration in copper; (4) Depth of surface imperfections, such as cracks, pits, and fabricating defects; (5) Depth and penetration of corrosion as well as any alteration in structure thereby produced; (6) Thickness of a protective coating, such as an electro deposit of nickel, copper, chromium, cadmium, or zinc; or of hot-dipped coatings, such as galvanized zinc coatings on steel; (7) Structure of the protective coating. (If the applied protective coating forms an alloy with the base metal as in the case of zinc with iron and tin with copper, then the structure and thickness of this intermediate layer can be determined provided the coating has been applied by the hot dip process, i.e., in a molten state.)

    5 The removal of carbon (usually in reference to the surface of solid steel) by the action of a media (normally oxidizing) which reacts with carbon is known as decarburization.

In the case of electro deposits the number and types of deposit can also be determined, since every time the plating process is interrupted and re-started, a line of demarcation appears even though the same metal is used. For example, if there are ten layers of copper deposits on a steel rod, then nine lines of demarcation will occur within the copper plate. (Figure 5.)
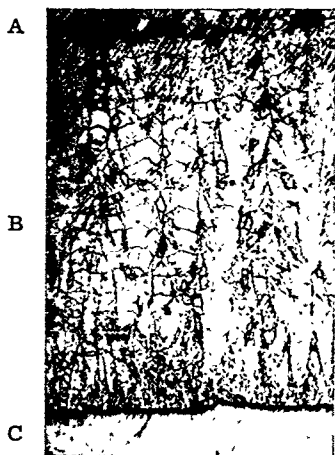
A

B

C

FIGURE 5

Transverse section of copper-plated stainless steel. The portion below the lower heavy black line is the stainless steel base (C) while the area (B) above is the copper deposit and area (A) represents the cast on mounting material. The fine irregular traverse lines in the copper deposit indicate the number of interruptions in the electro-plating process.

Longitudinal sections reveal in general the following information: (1) Extent of deformation of non-metallic impurities and the arrangement of the non-metallic inclusions and oxides; (2) Degree of plastic deformation as is shown by the amount of grain distortion due to such treatment as wire drawing; (3) Presence or absence of banding, that is, layers of different composition in the structure; (4) The perfection and uniformity of any heat treatment, as, for example, uniformity of grain size in copper and brass and the uniformity of structure in heat treated steel and alloys in general.

In reporting the results of a microscopic examination the location of the samples should be accurately stated, especially in describing the structure as shown by photomicrographs.

B. CUTTING THE SPECIMEN

Having decided upon the location and type of section, the next step in the preparation of metallographic specimens is that of cutting the sample.

During the cutting of the sample from the object submitted, care must be exercised to avoid changing the structure in any way. Heat treated alloys, such as steel, are very susceptible to heating effects and even careful grinding on an uncooled grinding wheel

may generate sufficient heat to induce structural changes. There-
fore, to minimize the heating effect, a copious supply of cooling
water should be used. During cutting, the cutting tool must be
sharp and should be well lubricated to minimize dragging of the
metal by the edge of the cutting tool.

Whenever possible the specimens for metallographic examina-
tion should be not more than ½ to 1 inch square and from ¾ to ¾
inch thick, for if the height of the specimen is greater than its
width, it becomes difficult to maintain a flat surface during polish-
ing. On the other hand, if the specimen is cut smaller, it is almost
impossible to polish the surface without producing excessive round-
ing of the edges. Of course, it is not always possible to obtain
samples of the most convenient size, and at times wire, sheets,
strips, fragments of metal, and other small objects must be mounted
either in clamps, fusible alloys, or in mounting plastics. In cases
in which it is not necessary to study the structure to the extreme
edge of the specimen, the edges may be beveled so as to prevent
tearing of the polishing cloth by the sharp corners.

When it is necessary to cut specimens from very large sections,
flame cutting must occasionally be resorted to but with the fol-
lowing strict precaution. The section thus removed must be suffi-
ciently large so that it can be re-cut to the proper size by some
other method. During oxy-acetylene cutting the intense heat gen-
erated completely obliterates any of the distinctive original struc-
tural peculiarities along the flame cut edge and its vicinity and
thus makes the results of any microscopic examination of these
areas worthless. This method is recommended only as an extraordi-
nary procedure to be used under expert supervision and with the
greatest care.

The following rules should be observed in connection with all
cutting procedures. Hard and brittle materials may be notched
and then fractured by means of a sharp blow. That part of the
section held in the jaws of a vise or clamp during the cutting
process is strained and deformed and should not be used for a
metallographic examination. Furthermore, before proceeding with
the polishing procedure all traces of oil and grease must be removed
by washing the specimen with lead-free gasoline, carbon tetra-
chloride (Carbona), or some other solvent. Rusty fractures may
be cleaned with a dilute solution of ammonium citrate or phos-
phoric acid. (Table I lists methods for cutting various metals.)

C. MOUNTING OF TEST SPECIMENS

When mounting test specimens, the purpose of the particular

micro-examination will in most cases determine the type and method of mounting. Among the more important factors which determine the type of mount selected are the size and shape of the specimen and the maximum temperature to which it may be subjected without bringing about changes in its microstructure. Of course, in many cases the equipment available for mounting will be influential in determining the procedure adopted. The methods of mounting test specimens can be conveniently divided into the following four groups: (1) Mechanical mountings; (2) Electroplated mountings; (3) Cast and cement-like compositions; (4) Thermo-plastic and thermo-setting materials.

(1) *Mechanical Mountings.* Various types of clamps are available for mechanical mountings. For specimens having straight sides, parallel steel clamps are quite satisfactory. Round specimens, which are sectioned transversely, may be held in certain circular type clamps, but longitudinal sections of round wire are usually best mounted in parallel steel clamps. When the extreme edges of the specimen are to be examined at either medium or high power, clamps are practically indispensable. In most cases it is possible to mount only one section in each clamp, which often requires handling an inconvenient number of specimens, but occasionally two or more specimens can be mounted together and the number of mounts thus reduced.[6]

---

[6] The laboratory technician will find the following considerations of importance when called upon to select clamps for mechanical mountings. The most satisfactory type of clamp to prevent rounding of the edges is one which has the same degree of hardness as the specimen being examined, and the degree to which the edges are rounded during polishing is proportional to the difference between the clamp and the specimen.

There are, however, other factors which must be considered aside from the relative hardness of the clamp material. In the first place, if the sides of the specimen are irregular, it will be difficult to obtain close and uniform contact, with the result that a trace of the etching reagent will be held in the crevices between the specimen and the clamp and may later gradually exude out, thus staining the etched surface. Fortunately, with steel this difficulty can be overcome by placing thin sheets of a softer filler material, such as copper, between the specimen and the clamp and, when several units, such as sheets, are placed in a single mount, this filler can be placed between these units as well. This process will not only increase close contact but will help to preserve any surface irregularities of the specimen.

Sheets which are to be mounted should first be tightly bound into a pack in order to prevent excessive occlusion of the etching reagent and the polishing abrasives. Pores and voids may be filled by immersing the pack in molton paraffin or separating them with a dense piece of blotting paper. The last procedure, however, has the disadvantage that the paper may hold abrasive which will gradually become dislodged, thus making subsequent polishing difficult.

Another factor which must be considered is the composition of the clamp. At times, clamps of a dissimilar composition interfere with the etching process, as, for example, stainless steel specimens mounted in ordinary carbon steel clamps, but in most cases the use of two kinds of metals will not affect the etching process.

(2) *Electroplated Mountings*. Strictly speaking, electroplating is not a mounting process, but an intermediate step practiced to prevent tearing off or rounding of the edges of small wires, fractures, or specimens of irregular contour which must be examined out to the extreme edge. Iron, steel, and the ferrous materials are generally copperplated, whereas the precious metals are frequently plated with silver, gold, or nickel, depending on the nature and the hardness of the metal or alloy being prepared for microscopic examination. The fractures and surfaces of non-ferrous materials such as copper, brass, bronze, and nickel are often plated with silver. A frequent and satisfactory procedure with copper and its alloys is either to copperplate or to first nickel-plate and then to copperplate.

The important fact to keep in mind in selecting the proper plating material is that it should be somewhat softer than the specimen which is to be studied in order that differential polishing of the material may not take place, thus obscuring the edge of the specimen. An equally important restriction is that the electroplate should not react electrolytically with the metal of the specimen.

(3) *Cast and Cement-like Compositions*. Low melting point alloys, sulphur, and cement-like compositions, such as sealing wax, litharge and glycerine, plaster of Paris, DeKhotinsky cement, and iron-ammonium-chloride cements, are used to mount certain types of specimens.

The specimen which is to be mounted is placed in a mounting ring and the mounting medium cast around it. A piece of brass or iron pipe ½ to ¾ inch in diameter and ½ to ⅝ inch high forms a convenient mounting ring. In selecting the mounting material some thought should be given to its resistance to attack by the etching reagent which is subsequently to be used on the specimen, as well as to the effect of any electrolytic action between the mounting material and the specimen at the point of contact. Furthermore, any heat effect or tempering action on the specimen that may result from the molten mounting material constitutes an equally important consideration in this selection. This consideration is especially important in the case of hardened steel and some heat treatable alloys.

With the usual types of steel the inter-position of copper sheets will not interfere with the etching process since the usual etching reagents, such as picric and nitric acid in alcohol, scarcely attack copper. Similarly, copper may be mounted in steel clamps, since ammonia plus hydrogen peroxide used to etch copper only attacks the steel to a slight extent. When acidic or other reagents are used, which attack the steel clamps, it may be necessary to remove the specimen from the clamp during the etching process.

Copper, brass, nickel, soft steel, iron, Monel metal and electro-plated objects can all be mounted in fusible metal alloys which are cast around the specimen.[7]

The fusible alloys in general, and especially Wood's metal, are desirable because of: (a) Their adaptability to a great variety of specimen sizes and shapes; (b) Their close contact between the specimen and mounting material, which prevents occlusion of the etching reagent with subsequent exudation and staining; (c) Their relatively low melting temperature, which permits use even for specimens subject to tempering; (d) Their inertness to etching reagents, such as picric acid in alcohol and some others; and (e) Their moderately good preservation of the flatness of the edges of the specimen.

(4) *Thermo-Setting and Thermo-Plastic Materials.* The fusible alloys have one disadvantage which at times is quite trouble-some: namely, that materials, such as Wood's metal, have a tendency to smear onto the specimen surface during the polishing process. This difficulty has perhaps more than anything else led to the use of the snythetic plastics as metallographic mounting materials. The synthetics may be divided into two groups: thermo-setting resins (i.e., those that "set up" into a more or less permanent and rigid state under the influence of pressure and heat), and

---

[7] When cast or cement-like mounts are employed, experience has shown that the following materials are the most advantageous. Ferrous metals and alloys can be mounted in solder composed of 50% tin and 50% lead (melting point approximately 425° F.). A more fusible alloy, known as Wood's metal, is frequently used because its lower melting point (154.4° F.) has less tendency to produce a tempering action. (The composition of Wood's metal is bismuth 50%, cadmium 10%, antimony 25%, tin 12.5%.) Yet another alloy (melting point 203° F.) used by some is composed of bismuth 52.5%, lead 31.5%, and tin 16%. Zinc castings have been successfully mounted in cadmium-zinc *eutectic* (melting point 508° F.) which contains cadmium 82.5%, zinc 17.5%. It has about the same etching and polishing characteristics as zinc base castings. This alloy should never be heated over 572° F. as at that point very poisonous fumes are liberated. Brasses have been successfully mounted in lead-tin alloys when the etching reagent which is to be employed consists of ammonia plus hydrogen peroxide.

When the fusible alloys are not available, sulphur may be used as a mounting material since it melts at 264° F. and is not attacked by most cold etching reagents. For this reason it forms a good mounting material for aluminum, magnesium, and their alloys. Sulphur has, however, one disadvantage which may be objectionable at times: that is, it may cause pitting of steel samples or tarnish copper base alloys. But by using the following procedure these effects may be overcome. A brass ring of convenient size is placed on a smooth steel plate and enough mercury poured in to form a pool about ⅛ and not exceeding ¼ inch deep. The specimen is pushed through the mercury with the surface which is to be polished down and held in this position. Molten sulphur, which solidifies rapidly, is then poured in the ring. After solidification the ring is slid to the edge of the steel plate, and the mercury collected in a glass or porcelain dish. The use of this method prevents the sulphur from coming into contact with the grinding and polishing surfaces and consequently prevents smearing. On the other hand, the specimen is not in contact with the brass ring, but the surface which is to be polished is level with the edge of the ring.

thermo-plastic resins (i.e., those that do not "set up" permanently under the application of heat and pressure, but will flow each time that the proper combination of heat and pressure are re-applied). The thermo-setting materials are characterized by the bakelites (the phenol-formaldehyde and the aniline-formaldehyde groups) while the thermo-plastic materials are characterized by the poly-styrenes and the methacrylates or Lucite groups. Both types may be readily molded, but the thermo-setting resins are somewhat harder. The only difference in handling the two types is that because of their tendency to flow the thermo-plastic resins must be cooled to 70°-80° C. before being removed from the mold, whereas the thermo-setting resins may be taken out just as soon as the proper molding cycle has been applied and the resin has "set up." The thermo-plastic resins are for the most part transparent, which makes it possible to polish down to a predetermined point on the specimen, a possible advantage in certain criminal cases. (See Figure 6.) However, because of their tendency to flow and because of their relative softness, polishing should not be pushed to the point where the sample gets hot or excessive rounding of the edges may occur.[8]
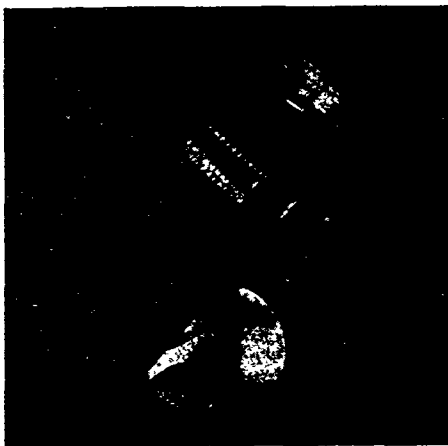
FIGURE 6

Typical Illustration of Transparent Synthetic Resin Mounting (Illustration and halftone, courtesy of Adolph I. Buehler, Chicago, Illinois.)

---

[8] In the use of thermo-plastic and thermo-setting materials, the following table showing the comparative properties of some synthetic resins may prove of value:

Thermo-Plastic Type	Brinell Hardness*	Hardness Comparable to
Poly-styrene I	19	
Poly-styrene II	22	Annealed aluminum
Methyl Methacrylate (soft)	17-20	
Methyl Methacrylate (hard)	27	Annealed copper
Thermo-Setting Type		
Aniline Formaldehyde	30	
Pheno Formaldehyde Plus Wood Flour	42	Semi-hard copper

(*Brinell hardness is obtainable by using 10 mm. ball and a 500 Kg. load.)
   Also see Wymann, L. L., "The Plastics for Mounting of Metallographic Samples," Proc. A. S. T. M. *38*, Part I: 511 (1938).

As far as the resistance to etching reagents of the two types of resins is concerned the thermo-setting resins are resistant to most materials, with the exception of strong oxidizing acids and strong alkalies. The thermo-plastic resins on the other hand may be only somewhat attacked by strong alkalies and strong oxidizing acids, but are generally quite soluble in organic solvents.

The equipment needed for processing the synthetic resin mounting materials may be obtained from the regular scientific supply houses. In using these types of mounting material the temperature and pressure should be controlled. The thermo-setting resins are generally heated to 140° C. for 8-12 minutes under a pressure of 2500 pounds per square inch. The thermo-plastic resins are usually subjected to the same pressure as the thermo-setting resins, but somewhat higher temperatures (145°-160° C.) are applied for a shorter time (6-7 minutes) and, as mentioned previously, must be cooled to a temperature of about 70°-80° C. before they are removed from the mold.

D. POLISHING THE SPECIMENS

(1) *Preliminary Facing or Rough Grinding.* The purpose of preliminary facing is to produce a flat surface which is suitable for the following steps in the polishing procedure and which will remove the rough, irregular, and distorted surface left by sawing or cutting. This may be accomplished by filing, on grinding wheels, on prepared papers, by machining, or on a motor-driven abrasive belt.[9] (Table I indicates the best means of surfacing various types of metals.) When this procedure is completed, however, there re-

---

[9] In filing, the specimen should always be pushed against the cutting edges of a mill file as rubbing both forward and backward tends to round the edges of the specimen. The file should preferably be gripped in a vise or held in a fixed horizontal position. Under no circumstances should the specimen be gripped in a vise during any of the polishing process as such procedure is liable to disturb the microstructure of the metal.

Grinding wheels produce satisfactory results in the hands of experienced workers. They may, however, produce rounded or grooved surfaces unless the wheels are frequently dressed in order to maintain a flat wheel surface. The sides of the grinding wheel should be kept clean, free from clogged metal, and sharp. When using a grinding wheel, heating of the specimen should be carefully avoided by keeping the wheel copiously supplied with cold running water. Speeds above 1200 R.P.M. are not recommended.

Endless motor driven abrasive belts have also been found to give satisfactory results, and this method has the advantage that it is not limited to specimens of a rather small size but can be used with large pieces of metal.

Regardless of the method of preliminary facing, however, the specimen under all circumstances should be kept cool and at all times care exercised to avoid deep scratches or gouges as these have been known to alter the structure of the underlying metal. especially in the case of metals and alloys susceptible to structural changes by comparatively slight cold working, as, for example, tin, zinc, and. lead.

main relatively deep scratches and microscopic grooves on the specimen resulting from the rough facing tool, and it becomes necessary to continue the polishing procedure with more refined methods.

(2) *Grinding.* The next step is known as grinding. The object of grinding is to reduce by means of progressively finer abrasives the tool scratches which were left on the surface of the specimen in the preliminary facing process until there remains only a series of very fine scratches which can be readily eradicated in the final or fine polishing operation. Grinding may be carried out by hand, using metallographic papers, or by means of the paper glued to power-driven wheels.[10]   (See Table I.)

(3) Rough Polishing. Rough polishing can be considered as the last step of the grinding operation. It consists of a further smoothing or reduction of the fine microscopic scratches left on the surface of the specimen. It is generally carried out on cloth-covered wheels with No. 600 alundum flour or similar material either as a watery paste or an aqueous suspension. (See Table I.) This operation is extremely important, since upon it depends the success of the final polishing. It determines in a large measure the actual

---

[10] When grinding by hand on abrasive papers, the specimen is rubbed with a reciprocating motion to and from the operator, using just enough pressure to keep it firmly in contact with the paper. The paper should be backed by a plane-smooth, hard surface of either metal or plate glass. When going from one grade of paper to the next finer, the specimen should be rotated through an angle of 90° as this makes it easier to determine when the scratches from the preceding paper have been removed. Even when all scratches due to the coarser paper have apparently been removed, grinding on the present grade should be continued for several minutes as an additional precaution to insure that the coarser scratches are completely obliterated.

When the papers are glued to power driven wheels the most important consideration is the linear velocity in feet per second (since it determines the cutting speed), and in order not to exceed the best working maximum linear velocity the wheel speed for a ten-inch disc should preferably be held under 600 R.P.M., although in some instances higher speeds have been successfully used. There must be no vibration. Hand grinding on abrasive papers is slower than machine grinding, but it has the advantage in that there is less heating and consequently less surface flow and distortion of the metal. In addition, hand grinding does not dislodge the non-metallic inclusions in steel which may in some cases be displaced by using power wheels.

A very important precaution during all of the various grinding and polishing operations is to completely wash all the abrasive from the specimen before going to the next finer grade. The specimen is then thoroughly dried. When using the cloth-covered polishing discs or wheels, a separate cloth, and, if possible, a separate head, should be used for each grade of abrasive. If it is not possible to use a separate head for each grade, then the new cloth should not be put on the disc until the polishing wheel has been thoroughly washed free from the previous and coarser abrasive.

Also see Rodda, J. L., "Preparation of Graded Abrasives for Metallographic Polishing," Trans. Inst. Met. Division, A. I. M. M. E. *39*: 149 (1932); Vilella, J. R., "Improved Method of Polishing Metallographic Specimens," Metals and Alloys *3*: 205 (1932); and Dowell, R. L. & Wohll, M. J., "Metallographic Grinding with Paraffin Impregnated with Abrasives," Metals and Alloys *4*: 181 (1933).

time required to complete the preparation of the specimen. If carelessly carried out, non-metallic inclusions in steel may be torn out, leaving a pitted surface, which gives a false impression of the cleanliness of the metal. If the rough polishing operation is rushed by exerting a heavy pressure or by forcing the specimen against the wheel, a relatively thick layer of flowed and distorted metal will be formed which must be removed before the true and representative structure of the metal is revealed.

(4) *The Final Polish.* The exact procedure used in carrying out the final polishing operation depends upon the purpose of the examination, but in all instances it is a wet polishing procedure which is carried out on cloth-covered rotating discs, or, when these are not available, by hand. Levigated alumina, magnesium oxide, and rouge are the usual abrasives. The first two are the most popular since they are cleaner to handle and do not stain the hands red. (Table I indicates some of the procedures to be employed in polishing common metals and their alloys.)

After the final polish is completed the sample should be free from scratches and when examined under the microscope should present a mirror-like and featureless surface, unless the constituents are of different colors or vary in hardness, or, when the metal is relatively porous. Excellent examples of variation in color of the constituents of the metal can be found in the case of ordinary commercial copper where the oxide is bluish and the pure copper salmon color; in cast iron, where graphite inclusions appear as black flakes, and in most aluminum alloys. When the constituents vary in hardness selective polishing will take place and one constituent will wear faster than the other, leaving the latter standing in relief. Copper again is a good example, with the harder oxide standing out in relief as well as being readily distinguished by its color. On the other hand, if the metal is porous, black spots and cavities will appear either over the entire surface or at least over a portion of it.

Microscopic examination at this point in the procedure is advantageous in determining the presence of inclusions, flaws and defects.

Polishing Precautions:

1. Presistent scratches which mar the polished surface are a question of cleanliness. The chief causes are dirty hands, abrasive grits under the finger nails, coarse abrasive particles adhering to the sides of the specimen, and a cloth contaminated by flying grit. The latter cause can be eliminated by keeping the wheel tightly covered and protected from flying grit when not in use. The remedy for the other defects is scrupulous cleanliness and thorough washing with warm water and a

TABLE I

Summary of Cutting and Polishing Procedures for Various Metals and Their Alloys

	Nickel	Iron and Steel	Precious Metals
Cutting	Hack saw or machining.	Hack saw, cutting-off wheel, or machining.	Hack saw or machining.
Preliminary Surfacing	File with light pressure.	Filing, grinding, or endless abrasive belt.	Flat, single cut file.
Grinding	Carborundum papers Nos. 180, 240, 320, and 400 by hand or glued on discs rotating at 300-600 R.P.M. Use light pressure. (No. 400 paper best if worn and graphited.)	On Nos. 2, 1, 00, and 000 metallographic papers or on wheels covered with paraffin-impregnated billiard cloth or canvas using abrasive grains Nos. 280, 320, and 400. Canvas cloths best for coarser grade abrasives.	Nos. 240, 280, 320, and 400 grain aloxite paper, followed by 000 and 0000 metallographic paper, which were smoothed by rubbing with a piece of hardened steel.
Rough Polishing	Billiard cloth covered wheel with a suspension of No. 600 alundum in water. Avoid excess water on wheel. Speed 300-400 R.P.M.	No. 600 emery (or finer) on paraffin impregnated billiard cloth covered wheel.	Well moistened felt covered wheel, using No. 600 alundum.
Final Polishing	To show micro-structure use billiard cloth covered wheel with levigated alumina settling at rate of ¾ to 1 inch per hour. To show inclusions use flat silk crepe cloth and levigated alumina.	Depends on purpose of examination. To study non-metallic inclusions use hard, pileless cloth on wheel, such as good quality cotton or linen cloth, dull side of heavy silk satin, or good flat crepe. For high power examination to study micro-structural details use softer cloth, such as "Kitten's Ear" broadcloth, with levigated alumina or fine magnesium oxide. Wheel speed 280-300 R.P.M.	Velvet covered wheel, using U.S.P. *heavy* magnesium oxide paste (made with distilled water) or levigated alumina, settling at a rate of 0.25 inch per hour.[1]

	Aluminum	Copper	Magnesium
Cutting	Hack saw or machining.	Hack saw or machining.	Hack saw or machining.
Preliminary Surfacing	Medium mill file.	Medium mill file or endless abrasive belt.	"Regular Cut" file followed by strokes on a "Second Cut" file.
Grinding	Nos. 0, 00, and 000 metallographic paper coated with a solution of paraffin in gasoline.	Nos. 0, 00, and 000 metallographic paper.	Nos. 1, 00, and 0000 emery papers. Kerosene may be used on papers to prevent fouling.

Rough Polishing	No. 600 alundum flour suspended in water; broadcloth covered wheel turning at 300 R.P.M.	600 alundum worked into paste with water on wheel covered with fine grade of broadcloth. Speed 500 R.P.M. Avoid excessive pressure and long contact with wheel. Having removed paper scratches, wash cloth free of abrasive with water. Hold bar of Ivory soap against wheel to make good lather. Hold specimen *lightly* against wheel (speed 300 R.P.M.) and move in direction opposite the wheel rotation until surface is bright and highly reflective.	(1) Turkish emery, No. 500 carborundum, or Nos. 400 or 600 alundum, depending on depth of scratches left by paper. No. 600 usually satisfactory. (2) Tripoli on a wool broadcloth wheel or two felt-covered wheels, one using "RF" and the second, "SF6X" emery.
Final Polishing	Merck's heavy magnesium oxide powder[2] well worked into wheel covered with "Kitten's Ear" broadcloth rotating at 150-200 R.P.M. Rotate through 90° frequently to reduce surface flow. Keep polishing cloth moist at all times with distilled water. As previous scratches are removed, wash cloth practically free of polishing material and hold specimen against the revolving polishing disc, using a copious supply of distilled water. Care at this point is essential to attain a good polish. Chemical composition and temper of the specimen determine the exact pressure to be used. After polishing is complete wash sample free of the last traces of polishing material in stream of tap water and dry by blowing the excess water from the surface. Do not rub or touch the polished surface.[3]	A water suspension of levigated alumina or finely powdered magnesium oxide on wheel covered with fine grade of wool or "Kitten's Ear" broadcloth rotating at 600-800 R.P.M. Use distilled water with magnesium oxide; work into cloth with fingers, pushing coarse particles to edge of polishing wheel. After removal from the final wheel the specimen may be etched immediately, or rinsed free from abrasive in warm water, washed with alcohol, dried quickly, and then etched.	Cover wheel with closely woven silk-velvet of short but full-bodied nap and work small quantity of Merck's U.S.P. *heavy* magnesium oxide into nap with fingers, using *distilled* water. Press specimen firmly against wheel (speed 150 R.P.M.) and rotate specimen in opposite direction of wheel two or three times. Reduce speed to 100 R.P.M. With very slight pressure rotate specimen in opposite direction of wheel 2-3 minutes.[4] Then flood wheel with distilled water to remove any remaining polishing powder from both cloth and specimen. (Complete removal of the polishing materials is expedited by slightly increasing the pressure of the sample against the wheel for a few seconds.) Quickly plunge specimen into hot distilled water, remove immediately, and dry with sharp air blast. (This procedure is superior to the alcohol rinse procedure.)

1 See R. H. Leach and C. H. Chatfield, Proc. Inst. Met. Div., A. I. M. M. E., p. 743-751 (1928).
2 The magnesium oxide used must be free from caustic or an undesirable etching effect will occur.
3 Specimens of most metals will retain their polish and brilliance for long periods of time if stored in a desiccator. See Dix, E. H., Jr., Chem. and Met. Eng., 27: 1217 (1922), and National Metals Handbook (1939).
4 See J. A. Gann, Trans. Inst. Metals Division, A. I. M. M. E., p. 309 (1929) and Dow Metal Laboratory Methods (1933), The Dow Chemical Co., Midland, Mich.; also Nat. Metals Handbook, p. 591 (1939).

mild soap, such as Ivory, when going from the coarser to the next finer grade of abrasive.

2. During all wet polishing operations the specimen should be slowly and constantly moved in the reverse direction opposite to the rotation of the polishing disc, and from the center to the circumference of the wheel. This will wear the cloth wheels evenly and assist in obtaining a uniform polish. The position of the specimen on each wheel is changed so as to polish with the next finer abrasive at right angle to the scratches left by the preceding coarser abrasive, that is, rotate the specimen through 90° before polishing with the next finer abrasive. If the metal is porous, the specimen should be rotated on its own axis during polishing in order to prevent forming "comet tails." This is generally a good practice to follow, especially on the last polishing wheel.

3. Rocking or uneven pressure will cause a rounding of the surface which is being polished and will destroy surface features. Under microscopic examination a round surface cannot be sharply focused over the entire field of view and consequently will yield "fuzzy" and "foggy" looking photomicrographs.

4. The preliminary surfacing, grinding, and paper work are of tremendous importance and should not be hurried or carelessly performed, because they are among the earlier steps in the polishing procedure. Any imperfections in these will not be removed by the final polishing operations. If the early work has been neglected, the surface after the final polish will be in a severely distorted condition, and upon etching will develop cross marks, scratches, or even a general surface roughness, which will obscure the true structural details of the metal. Observations made on an improperly prepared surface have no significance other than to indicate that some stage of the polishing procedure has been improperly carried out. The forced polish left by buffing is unsuitable for microscopic work since it leaves the surface badly distorted and smeared.

5. When using magnesium oxide as the final polishing material, distilled water must always be used. Ordinary tap water results in the formation of hard abrasive particles, magnesium carbonate, which can produce deep scratches and ruin the final polish. If magnesium oxide has been used as a final polishing abrasive, upon completion of the work the cloth should be thoroughly washed with distilled water.

6. New polishing cloths should be boiled in distilled water for several hours to soften their fibres. This step is especially desirable when polishing the softer metals and alloys. When not in use the cloths should be kept in distilled water containing a slight concentration (about 2%) of hydrochloric acid, especially if magnesium oxide has been used as a final polishing medium. If the cloths are left exposed to the air, they will harden and cake due to the absorption of carbon dioxide from the atmosphere.

7. If it is necessary to interrupt any of the wet polishing steps even for only a few minutes, the sample should be thoroughly washed and dried. If left wet, iron and steel samples will corrode and become pitted, while non-ferrous metals and alloys may discolor or corrode.

E. ETCHING

During the polishing process a thin layer of flowed metal is formed on the surface of the specimen. In order to reveal the true structure of the metal or alloy this layer must be removed by treating the surface with a chemical reagent. This process is known as etching.

Etching is primarily a differential chemical attack on the various constituents which are present in a metallic aggregate. The value of a good etching reagent lies in the fact that it will develop the structure as it actually exists. The action of the etching reagent must not be too drastic or the contrast between the various constituents will be destroyed. The degree of activity can be con-

trolled by using solutions of various concentrations, and it is a very rare occurrence when a concentrated etching reagent is employed where it is desirable to develop in detail the fine microstructure of the metal.

The structure of a metal, as it is seen under the microscope, is dependent upon its chemical composition as well as its thermal and mechanical treatment. Generally, a pure metal presents a polygonal structure for although the metal is quite pure the surface will not be uniformly attacked by the etching reagent. Because of the random orientation of the crystals in a metallic aggregate various faces of the crystals are exposed to the etchant, and since some are more readily attacked than others a difference in level results between the crystals, the boundaries between them showing up as dark lines. Still a further effect of the etching reagent is to roughen the surface of the crystals and in some cases to form an oxide or a film on the surface. If the etching is continued for some time, microscopic valleys will actually develop at the grain boundaries. This differential attack on the crystals, which is dependent upon the particular crystal facet which is exposed, causes some crystals to appear lighter than others. The variation in brightness over the surface of the specimen is due to the resulting unevenness of the metallic surface after etching, which causes light to reflect from each crystalline face at a different angle. Those crystals which have their surfaces so situated as to reflect the light up into the microscope tube to the eye will appear bright, whereas those whose surfaces reflect the light outside the microscope will appear dark. Because this effect depends upon the orientation or arrangement of the crystals, it is known as oriented lustre.

If an alloy is composed of two or more elements which produce a structure different from that of the pure metal, it may be identified by the peculiar form or structure exhibited. Very frequently the constituents of an alloy will be stained a characteristic color, and by this means the elements of some alloys are recognized.

For metallographic work two types of etchings are used. The first, macro-etching, is employed to reveal the gross structure of the metal to either the naked eye or by examination with low-magnification (generally below 10X). (Figure 1 is an excellent illustration of macro-etched surfaces.) The second type, micro-etching, is employed to reveal the micro-structure or fine details of the metal for examination at intermediate and high-magnifications. (The re-

sult of such an etching procedure is illustrated in Figure 3.) In preparing the surfaces for macro-etching it is generally not necessary to proceed beyond the grinding steps (i.e., to proceed beyond dry finishing of the surface), but for micro-etching, the specimen is usually completely polished.[11]

---

[11] Before etching, the sample should be thoroughly cleaned and dried, and while being immersed in the etching reagent it should be kept in motion or swabbed with cotton. This procedure keeps a fresh portion of the reagent in contact with the sample at all times and removes any gas bubbles which may form as the result of the chemical attack, thus producing a more uniform etch.

The degree of etching must be carefully controlled and is generally accomplished by varying the time of etching, since for most routine inspections the manner of attack of the combinations of chemicals used is fairly well known. For examination at high magnification the degree of etching should be lighter than for low power work since an etch suitable for low power (75-200 diameters) produces too much relief and thus makes sharp definition practically impossible at 500 diameters or above. It is therefore generally advisable to start with a light etch, completing first the high power examination, and then to etch somewhat deeper for the low power work. This procedure will prove time saving for in order to perform an examination at high power after the specimen has been etched for low power work, it is necessary to go back to the No. 0 paper and completely repolish. If the high power work is done first, repolishing is obviously unnecessary.

Deep etching or over etching is to be avoided, and, if necessary, it is better to repeat the etching process several times than to over etch. In the case of stainless steel it may be necessary to polish, etch, repolish, and re-etch several times in order to remove completely the distorted metal produced by grinding and polishing and to expose finally the true structure. Aluminum and its alloys may also have to be repolished and re-etched once or twice to get fine definition.

In some cases, especially when two constituents are present, greater contrast can be obtained if a combination etch is used. For instance, when alpha and beta structures are present as in 60-40 brass, a ferric chloride etch following the regular ammonia-hydrogen peroxide etch adds contrast by darkening the beta constituents. In the case of phosphor bronze and copper, beautiful coloration and contrast can be obtained by following the ammonia-hydrogen peroxide etch by a few seconds of electrolytic etching. When studying the copper-beryllium alloys, much better results are generally obtained if a light etch of potassium bichromate precedes the electrolytic etch.

Electrolytic etching has much to commend it since considerable variation is possible by varying both the time of etching and the current density. This type of etching is particularly suited to the etching of tungsten, copper-nickel, copper-tin, and Monel metal.

Even when the entire polishing procedure has been properly carried out in every detail, there may be on the polished surface a thin layer of flowed or distorted metal. There is no better way of removing this layer than by alternate polishing and etching and this may be carried out as follows: The polished specimen is given a normal etch and the structure examined under the microscope, using the highest resolving power dry objective available. After this the sample is repolished on the final wheel, re-etched, and re-examined. This process is repeated as long as any changes appear in the structure. Normally one or two and not more than three repolishings are sufficient, but with soft metals more may be necessary. The procedure of deep etching sometimes used as an attempted short cut usually results in pitting and obliteration of the fine structural details.

For more extensive lists of reagents than appear in this paper, see Vilella, J. R., "Metallographic Technique for Steel," Am. Soc. Metals (1938); National Metals Handbook (1939); and the articles by the author in the General Electric Review 28 (8): 573 (1925) and 28 (11): 800 (1925); and in Wire and Wire Products 11 (8): 378; (9): 430 and (11): 648 (1936).

Etching Techniques for Commonly Used Metals:

Aluminum. For the macro etching of aluminum a Tucker's[12] or Flick's[13] etch is perhaps the most useful, and satisfactory results are usually obtained when the reagent is applied to a smooth and well-ground surface. Either swabbing or immersing the specimen in the etchant is suitable, but unless the specimen is too large the latter is to be preferred. After etching the excess reagent is thoroughly washed from the surface and the speciment completely dried. For micro-etching either the 0.5% hydrofluoric acid etchant or 1% sodium hydroxide is generally the most useful and they are applied with a swab of soft absorbent cotton on a physician's applicator. The time of etching is about 10-15 seconds. This method gives uniform and satisfactory results and yields a surface suitable for photographing. The majority of the other reagents are useful for specific purposes, such as the identification of compounds or for revealing the grain structure of certain alloys:[14]

The following precautions should be observed in order to obtain the best results in etching aluminum and its alloys. Whenever etching by the immersion method specimens should not be held with metallic laboratory tongs as electrolysis which affects the etching rate may occur. Furthermore, it is extremely important to control both the temperature of the reagent and the specimen as well as the time of etching, while only the recommended concentrations of the reagents should be used. After etching is completed the excess reagent should be removed by washing in a stream of water, followed by rinsing in absolute alcohol and drying by a jet of air. The micro-constituents of aluminum alloys are first and best studied on the polished surfaces and then by a systematic etching procedure.[15]

Copper. In macroscopic examinations, after the surface is prepared by grinding, rough polishing, or by cutting with a fine, well-sharpened tool, either a saturated solution of chromic acid, ferric chloride,[16] 20-50% nitric acid, or 20% ammonium persulphate is applied as the etchant either by swabbing with cotton or immersion.

For micro-etching of copper, ordinary (alpha) brass, and other copper alloys, ammonia plus hydrogen peroxide are the most generally used reagent. The proportions employed vary with the copper content of the specimen. Pure copper is etched with five parts (by volume) of ammonia, and five parts water, plus two parts hydrogen peroxide (9%). (Fresh hydrogen peroxide is necessary for best results.) However, when etching brass containing 65% copper, only one part hydrogen peroxide (9%) is added to the ammonia and water. When etching pure beta brass, the ammonia-hydrogen peroxide etch is usually followed by a ferric chloride etch to darken the second (beta) constituent.

---

[12] Tucker's reagent is composed of hydrofluoric acid 15 cc., hydrochloric acid 45 c.c., nitric-acid 15 c.c. and water 25 c.c. The specimen is immersed in the reagent. See also Tucker, C. M., Metals and Alloys *1* (August): 655 (1930).

[13] When using Flick's reagent the sample is immersed for 10-20 seconds, washed in warm water, followed by a dip in nitric acid. The reagent is prepared as follows: hydrofluoric acid 10 c.c., hydrochloric acid 15 c.c., and water 90 c.c. See Flick, F. B., "Etching Aluminum and Its Alloys for Macroscopic and Microscopic Examination," Trans. A. I. M. M. E. *71*: 816 (1925); Corson, M. G., Aluminum and Its Alloys, D. Van Nostrand Co., Inc., N. Y. City (1936) 239; Anderson, R. J., "Metallography of Aluminum," Chem. & Met. Eng. *17*: 64, 172 (1928); and Hanson, D. and Archbutt, S. L., "The Micrography of Aluminum and Its Alloys," Jr. Inst. Metals (British) *21* (1): 291 (1919).

[14] Dix, E. H. and Keller, F., Mining & Metallurgy *9*: 327 (1928); also see references cited in footnotes 12 and 13.

[15] An excellent order of procedure for such examination is given by Dix, E. H. and Keller, W. D., Proc. A. S. T. M. *26*: part II (1926); and also Keller, F., Jr. and Wilcox, G. W., Metal Progress *23* (April): 45 (1933).

[16] Ferric chloride is used either for macro-etching or to give contrast following other bright etches such as chromic acid. The writer has found that a reagent consisting of 25 grams ferric chloride, 25 c.c. hydrochloric acid, and 100 c.c. water is a good general reagent for macro-etching copper and many of its alloys. The ferric chloride may be varied from 1 to 25 grams per 100 c.c. of water and hydrochloric acid from 6 to 50 c.c. See also Rosenhain, W., Introduction to the Study of Physical Metallurgy, D. Van Nostrand Co., Inc., N. Y. City (1914).

Sometimes a combination etch must be used to obtain contrast or the correct coloration of two or more constituents. For example, copper and phosphor bronze can be very beautifully colored if the ammonia-hydrogen peroxide etch is followed by an electrolytic etch for 2-5 seconds.[17] (If this procedure is followed the etched surface must not be swabbed, but is dried quickly by an alcohol rinse, or a blast of hot air.)

As a rule, the alloys of copper with manganese, silicon, beryllium, etc., can be satisfactorily etched with the bichromate reagent,[18] whereas the ammonia-hydrogen peroxide etchant is inferior. The bichromate etch can also be used for leaded brass rods, Tobin bronze, and alloys of copper with nickel. As an alternative the copper-beryllium alloys can be etched by first etching slightly with potassium bichromate and then following this by the ferrous sulphate electrolytic etch.

Whenever specimens of copper and its alloys are etched, the following instructions are to be observed. After etching the specimen should be washed with running water, rinsed in absolute alcohol, and dried with an air blast. The etched surface may be preserved from tarnishing by coating it with a thin layer of oil or glycerine or for permanent protection with a clear, transparent lacquer. At times it is desirable when etching for microscopic examination to hold the specimen with platinum tipped forceps, rather than ordinary nickel tongs, especially if the more corrosive reagents are used.

The time required for etching copper increases with the amount of annealing given the material, and decreases with the degree of coldworking.

Iron and Steel. The most generally useful reagents are dilute solutions of picric acid and nitric acid in alcohol.[19] When it is necessary to detect the various

---

[17] A satisfactory electrolytic contrast etch, useful for bronze, nickel-silver, and other copper alloys is composed of ferrous sulphate 30 grams, sodium hydroxide 4 grams, sulphuric acid 100 c.c., and water 1900 c.c. The sample is the anode and platinum or stainless (18-8) steel is used as the cathode. Apply 0.1 ampere at 8-10 volts D.C. See also Hudson, O. F., Jr. Inst. Metals (London) *13*: 193 (1915) and Desch, C. H., Metallography, Longmans, Green & Co., N. Y. City (1913 and 1937).

[18] The bichromate etch is prepared as follows: potassium bichromate 2 grams, sulphuric acid 8 c.c., sodium chloride (saturated soln.) 4 c.c., water 100 c.c. See Strauss, Jerome, Chem. & Met. Eng. 28 (19): 852 (1923) and Vilella, J. R., "Delving Into Metal Structures," The Iron Age, *117*: 761, 834, and 903 (1926).

[19] The picric and nitric acid reagents are prepared as follows, and reveal the structures noted:

Nitric Acid (Nital)—Nitric acid (sp. gr. 1.42) 1.5 c.c., ethyl alcohol (95% or absolute) 100 c.c. Etching rate is increased, selectivity decreased, as the per cent nitric acid is increased. 4% in amyl alcohol useful to develop grain boundaries and contrast in low carbon materials. Etching time a few seconds to a minute. Used on carbon steels (1) to darken pearlite colonies, (2) to bring out Ferrite (iron) grain boundaries clearly, (3) to differentiate Ferrite (iron) from Martensite (a structure found in heat treated steel). For cast iron, carbides are unetched.

Picric Acid (Picral)—Picric acid (clean, dry crystals) 4-5 grs., ethyl alcohol (95% or absolute) 100 c.c. (Use *absolute* alcohol only when crystals contain 10% or more of moisture). This reagent is superior to "Nital" except for specific uses listed above. "Picral" shows detail more delicately than "Nital," but does not reveal grain boundaries as readily as "Nital." Etching time a few seconds to a minute or more. Used for all grades of carbon steel in the (1) annealed, (2) normalized, (3) quenched, (4) quenched and tempered, (5) spherodized, and (6) aus-tempered condition. Also useful for all low alloy steels attacked by this reagent.

A saturated solution of ferric chloride in hydrochloric acid to which a little nitric acid has been added is used to develop the structure of stainless steel. This reagent is used full strength. With many of the stainless irons and steels the method of alternate polishing and etching must be used. The 18-8 and other alloys can be etched by means of the following reagents: nitric acid 10 c.c., hydrochloric acid 20-30 c.c., glycerol 20-30 c.c. (The specimen is warmed in water before etching.) This reagent is also useful for high-speed steel. However, in the totally austenitic stainless alloys such as 18-8, the following reagent gives better results: nitric acid 10 c.c., hydrochloric acid 20 c.c., glycerol 20 c.c., and hydrogen peroxide

carbides in steel, however, various alkaline etching reagents are employed,[20] while cupric chloride reagents are used to reveal phosphorous segregation.[21]

At times a piece of steel can be identified by identifying its various inclusions.[22]

In etching iron and steel specimens the time and temperature must be carefully controlled, and the specimen should be kept in motion while immersed to prevent gas bubbles from clinging to the surface and causing a non-uniform etch. When the etching is complete the specimen should be thoroughly washed with warm water, immersed in absolute alcohol, and dried in a warm air blast. Once etching is completed the specimen must not be rubbed.

The most useful reagents for macro-etching are 50% hydrochloric acid[23] and various concentrations of nitric and sulphuric acids. When examining iron and steel for surface defects such as seams, laps, fins, grindings, cracks, etc., special preparation is not needed, since the etching reagent will remove surface deposits such as scale. For revealing defects in the interior of a bar a section, of course, must be prepared. When using hydrochloric acid a machined surface is sufficient, but some reagents, such as Humfrey's, Le Chatlier's, 10-20% ammonium persulphate,[24] etc., require a well-polished surface for best results.

---

10 c.c. The speed of etching can be varied by varying the amount of hydrochloric acid. (For special alloys the hydrogen peroxide can be replaced by an equal quantity of acetic acid.)

Ten grams of oxalic acid in 100 c.c. of water may also be used as an electrolytic etch. The specimen is the anode while the cathode is of stainless steel or platinum, the two being about one inch apart. The voltage varies between 6-30 volts and the time from 10 seconds to one minute, depending on the structures that it is desired to reveal. See Ellinger, Trans. A. S. M., 24 (1): 28 (1936) and Arness, W. B., Trans. A. S. M., 24: 701.

[20] Sodium Picrate (Alkaline)—Picric acid 2 grams, sodium hydroxide 25 grams, water 100 c.c. This reagent may be used boiling (10-15 minutes), but preferably electrolytically at room temperature. The specimen is anode, cathode is platinum or stainless steel. (Six volts D.C., 40 seconds generally sufficient.)

The etchant attacks sulfides and colors Cementite (iron carbide), but carbides high in chromium (in tungsten steel), iron tungstide (Fe_nW), and iron tungsten carbide (Fe_4W_2C) are colored more rapidly than Cementite, but tungsten carbide is unattacked. It outlines grain boundaries in steels containing more than 0.80-0.90% carbon in the slowly cooled condition.

[21] The phosphorous reagent is made as follows: cupric chloride 1 gram, magnesium chloride 4 grams, hydrochloric acid 1 c.c., water 20 c.c., alcohol (absolute) 100 c.c. (Dissolve salts in least possible quantity of hot water.) Etching time is one minute, which is repeated if necessary.

This reagent is used to show phosphorous segregation or other elements in solid solution as copper tends to deposit first on areas lowest in phosphorous.

[22] Wohrman, C. R., "Inclusions in Iron," American Society for Metals, Cleveland.

[23] The 50% hydrochloric macro-etch consists of equal parts of acid and water and is used hot (160-175° F.) for from 15 minutes to ½ hour, depending on the steel, to reveal flow lines, cracks, porosity, and dendrites. A good universal macro-reagent consists of hydrochloric acid 500 c.c., sulphuric acid 70 c.c., water 180 c.c., and is used at 160-175° F. for from 1-2 hours.

Strain lines and obliterated numbers on firearms may be restored by means of Fry's reagent, which is cupric chloride 90 grams, hydrochloric acid 120 c.c., and water 100 c.c. At times the contrast may be increased by reducing the cupric chloride to 45 grms. and increasing the hydrochloric acid to 180 c.c.

It is most useful for mild steel, particularly Bessemer Steel, and when so used it may be necessary to heat the specimen 5-30 minutes at 300-475° F., depending on the condition of the steel. During etching the surface should be rubbed with a cloth soaked in the etching solution, and after etching washed in alcohol or rinsed in 1:1 HCl to prevent copper deposition. When it is used to restore obliterated numbers on firearms, the etching time may run into hours. The reagent should be applied to a finely. ground or polished surface. Also see Yatsevitch, M. G., "The Macro-Examination of Steel," Army Ordnance, January and February, 1931.

[24] The grounded or polished surface should be rubbed with absorbent cotton dipped in a freshly prepared solution. (Etch ½ minute or more.) This reagent is particularly good for welds.

Whenever the hydrochloric acid etchant is used on steel, best results are obtained with a fresh solution at a temperature at about 160° F. This reagent must be used under a hood since the fumes are very corrosive. Before beginning to etch the specimen it should be carefully washed either in soap and water or gasoline to remove grease and dirt and then heated in hot water to 160° F. This procedure makes it much easier to duplicate conditions and to control the time element since both the specimen and the etchant are then at the same temperature.

With all reagents the actual time of etching varies for different steels and even for the same steel in various conditions. For example, in the annealed state the time may vary from 15 minutes for the plain carbon steel to 45 or 60 minutes for the highly alloyed steel, such as nickel-chromium, nickel-chrome-vanadium, tungsten, and high speed steels.

After the specimen is etched, it should be removed and washed entirely free from acid in running water. The black "smut" deposited should be thoroughly scrubbed off with a stiff bristled brush. The specimen may be either blotted dry after washing or dried by an air blast or live steam. If it is to be preserved for some time, it should be completely freed from acids by placing it in plain boiling water or boiling water containing a little soda, followed by several rinsings in hot water. For permanent protection the surface should be coated with transparent lacquer or collodion. If the sample is to be photographed, the contrast can be increased by coating the surface with a thin film of glycerine.

Magnesium. The glycol etchant[25] is perhaps the most useful reagent for the present day magnesium alloys. Its value lies in the fact that it clearly delineates the various structural constituents of magnesium alloys and makes their identification positive. It is mild in its action and does not severely attack or pit either the alloy constituent or the matrix.

A convenient method of applying the reagent is to pour the etchant into a watch glass or small porcelain evaporating dish, and with a sliding motion immerse the specimen face downward. The specimen must not be allowed to touch or scrape on the bottom of the receptacle, and should be moved around in the etching solution to insure thorough and uniform wetting of the surface and to dislodge any gas bubbles which may form. The time of etching is 10-15 seconds but under some conditions this may be extended to 30 seconds. After obtaining the desired etch, remove the sample from the reagent, blow on the polished surface to remove any gas bubbles and the excess etching reagent, and then plunge it into boiling water.

Nickel. Nickel, monel and cupro-nickel and other nickel are best etched with nitric acid plus glacial acetic acid,[26] or with an electrolytic etch.[27] Over-

---

[25] The composition of the glycol reagent is diethylene glycol 75 c.c., distilled water 24 c.c., concentrated nitric acid 1 c.c. (Etch either by immersion or swabbing.) If diethylene glycol is not available, 5% citric acid in water may be used and applied in the same manner. Oxalic acid (2%) has also been used, and for macro-etching 10% solution of glacial acetic acid in water is satisfactory. (Apply the last two by swabbing.) When etching is completed rinse in warm water and then immerse in acetone and dry in a warm air blast. The time varies from 2-5 seconds for the oxalic acid etch up to 2 minutes for the acetic acid etch. Also see Gann, J. A., "Treatment and Structure of Magnesium Alloys," Trans. Inst. Metals. Div. A. I. M. M. E. p. 309 (1929).

[26] Flat Solution—Nitric acid (Conc.) 10 c.c., acetic acid (glacial) 50 c.c. (Prepare fresh daily and use only colorless nitric acid to prevent staining.) Etch by immersion for 5-20 seconds at room temperature. Dilute with 25-50% of acetone when etching alloys with less than 25% nickel.

[27] Electrolytic Contrast Solution—Nitric acid (Conc.) 10 c.c., acetic acid (glacial) 5 c.c., water 85 c.c.

Use 1.5 volt dry cell, with platinum wires, and etch for 20-60 seconds. Excellent for grain size studies, gives good contrast, and stains less than flat solution. The writer has found that the addition of 2-3 c.c. of phosphoric acid greatly reduces the tendency of staining and still gives good contrast.

The optimum amount of phosphoric acid will also vary with the condition of the cupro-nickel (i.e., with more extensive cold work more phosphoric acid may be used.)

etching of nickel and its alloys will invariably lead to pitting. After etching it is especially necessary with nickel to wash thoroughly with water, rinse in alcohol, and dry quickly with a clean air blast. The electrolytic contrast solution will stain less than the flat solution, and if a few stains develop with the flat solution, these may usually be removed by gently wiping the surface with clean, soft linen or cotton cloth. When the specimen has been severely cold worked as by rolling, deep drawing, etc., good results will only be obtained with the flat solution, and it also gives best results when studying the specimen for inclusions, flaws, and porosity. However, grain size uniformity is best studied by means of the electrolytic etch.[28]

Precious Metals. The precious metals are more difficult to etch than the other metals. The usual procedures and precautions must be carefully followed.[29]

EXAMINATION OF SPECIMENS—SURFACES TO BE CONSIDERED

When should the technician begin his microscopic examination? Should he examine the polished surface or defer the examination until the etching process has been completed? The illustration shown in Figure 7 indicates the advisability of pursuing a practice of examining the surface before as well as after it has been etched.

A   B

FIGURE 7

An illustration of the value of making a microscopic examination both before and after etching.

(A) An unetched (though polished) longitudinal section of a piece of flat copper strip containing a surface defect known as a sliver. The black particles represent copper oxide which was present in the metal in an excessive amount.

(B) The same longitudinal section after being etched with ammonia plus hydrogen peroxide. Although the defect in the metal is still visible, and although the etching reagent developed the small, uniform grain size of the specimen, it practically obliterated the oxide particles. Nevertheless, this characteristic appearance of the surface after etching is significant and valuable as an indication that the metal had been properly processed during fabrication and that it had been softened or annealed after rolling.

---

[28] Nitric Acid (30%)—Nitric acid (conc.) 30 c.c., water 70 c.c. is a good macro-etch for nickel-silver. (Etch by immersion.) Also see Mudge, W. A., "Etching Solutions for Nickel and Nickel Alloys," Nat. Metals Handbook ;and Adcock, F., "Internal Mechanism of Cold Work and Recrystallization in Cupro-Nickel," Jr. Inst. Metals (British), 27: 74 (1922).

[29] Platinum and palladium are etched by means of aqua regia and concentrated nitric acid respectively. Gold and its alloys are etched by using equal parts of 10% potassium cyanide (*Poison*) and 10% ammonium persulphate solutions. (Etch ½ to 3 minutes.) Also see Carter, F. E., "Platinum Metals and Their Alloys," Proc. Inst. Met. Division A. I. M. M. E. p. 766 (1928).

Silver and silver alloys may be etched by means of the following reagent: Potassium dichromate (saturated sol.) 100 c.c., sodium chloride (saturated sol.) 2 c.c., and sulphuric acid (conc. sol.) 10 c.c. For use, take one part of this solution and 9 parts of distilled water and apply by swabbing.

A and *B* of that illustration represent, respectively, the unetched and etched surfaces of the same longitudinal sections of a flat copper strip containing a surface defect known as a sliver. It will be observed that although the etching reagent did develop (in *B*) the small, uniform grain size of the specimens, it practically obliterated the oxide particles (shown in *A*), which were indicative of the presence in the metal of an excessive amount of oxide.
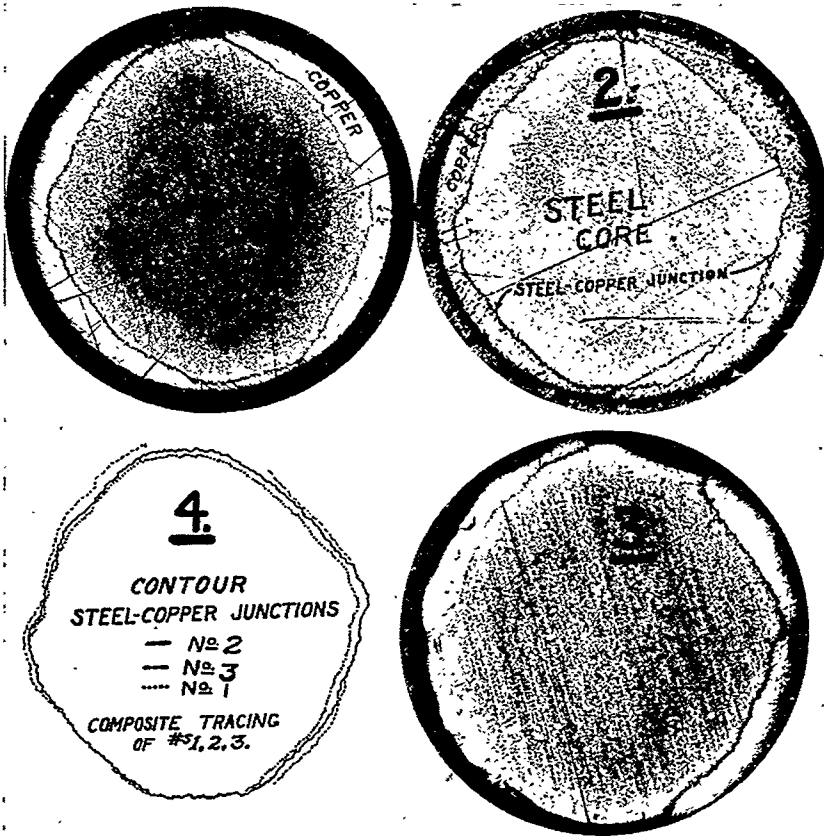

FIGURE 8

Copper-coated steel wire cross sections examined as part of the evidence in the Valier Coal Mine Bombing case. *1* and *2* are cross-sections from opposite ends of a small piece of wire (.486" in length) cut from a specimen of wire found in the workshop of the suspects in this case. *3* is cross-section of wire on the bomb timing mechanism adjacent to a cut and fracture end which in its physical appearance matched the ending of the wire in the suspects' workshop. *4* is composite tracing of copper-steel junctions *1*, *2*, and *3*, revealing that the junctions of all three specimens are identical in their lower portions and very similar throughout the remainder. (The average diameter of *1* was consistently smaller than *2*; and *2* consistently smaller than *3*.) See Wilson, C. M., *op. cit. supra* note 3 at p. 3.

As previously stated, it is an unwise practice to confine the microscopic examination to either a transverse or a longitudinal section of the specimen. It is far better to examine both types of sections. In most instances the dual examination will reveal two sorts of evidentiary matter—one confirmatory of the other. In some instances, however, one type of section will fail to disclose the desired information, whereas the other will be very productive of significant results. A typical example of the latter situation is furnished by a bi-metallic wire examination. A transverse sample of bi-metallic wire will be much more helpful for identification purposes than a longitudinal section. Consequently, if a technician relied solely upon a longitudinal section and neglected the examination of a cross-section sample he might be defeated in his attempt at effecting an identification. For instance, see Figure 8, an illustration from an actual case in which a comparison between the contours of the steel-copper junctions in two pieces of steel-core copper-coated wire yielded valuable evidence bearing on the question of the identity of the two specimens of wire. In this case longitudinal sections would not have been very helpful because the varying thicknesses of the copper coating would appear comparatively uniform in the longitudinal plane.

In concluding this discussion it might be of advantage to review briefly some of the types of cases to which the metallurgical technique is applicable, and also point out some of its limitations.

Like other procedures, metallurgical technique does not offer a universal solution for every case in which a metallic object is involved. For example, suppose a blasting cap becomes accidentally admixed with some coal, and that on tending the furnace the portion containing the explosive is thrown on the fire, with a resulting fatal explosion. The finding of small pieces of copper and copper wire is in this case not sufficient reason for an extensive microscopic and metallurgical examination. The circumstances surrounding the case determine the procedure to be adopted, and in this case an explosives expert would be decidedly more useful than a metallurgist. If, however, a fabricated bomb is thrown or set off and pieces of metal are found in the evidence, then these should be carefully collected and preserved, and compared with similar pieces which might be found in the possession of a suspect. The two cases referred to previously are good examples. Other types of cases where metallurgical procedures are useful are (1) the bursting or explosion of fire arms, (2) the unexplainable and sud-

den failure of machine parts, (3) elevator accidents, such as failure of the hoisting cables, and (4) in any case where the question of fixing liability for a failure is essential, or where malicious acts are suspected.

Recently the writer was asked to examine a burst revolver cylinder. There was no fatality, but the questions to be answered were (1) was the cylinder defective, or (2) since reloaded ammunition was used, was a heavy powder charge introduced into the cartridge case. In this case three sections were prepared for microscopic examination, a cross-section taken at right angles to the plane of fracture, and two longitudinal sections. One of these was in the plane of the fracture and the other at right angles to the plane of fracture. The value of supporting evidence is also demonstrated by this case, for in addition a chemical analysis was made, together with an examination of the gun by a firearms identification expert. All the evidence collected pointed to the conclusion that the metal was in no way defective.

The important point to bear in mind is that metallurgical techniques, like other procedures, are not always in themselves sufficient to establish the identity between two pieces of metal. Neither should every metallographic examination be expected to result in establishing the identity between two metallic objects. As with other evidence, the more data that can be collected, the more complete will be the evidence, and in addition the value of the individual pieces of evidence will also be enhanced thereby. Although it is possible that non-identity will be found in more cases than identity, it is always well to have a metallographic examination performed where the importance of the case justifies this and where it is advisable to know the answer, even if it is negative. If this policy is adhered to, the possibility of overlooking valuable evidence will be minimized. In some cases the negative answer may be valuable in refuting the evidence of the opposition and will thus serve a very useful purpose and justify the expense incurred in obtaining it.