"Shadow-cast" Replicas for Use in the Electron Microscope

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Metallographic specimens whose surfaces are to be investigated are too thick to allow either light or electrons to pass through them for microexamination by transmission. This difficulty is overcome with optical microscopes by illuminating the surface through the objective lens. For electron microscopes best results are obtained by preparing thin replicas of the surface of the specimen, placing them in the microscope and passing the electron beam through them.

Since electron microscopes represent a rather recent invention, they have found little application as compared with optical microscopes. This is true because, aside from the cost of new equipment and development of new techniques, some of the older replica methods necessitated the destruction of the surface from which a thin transparent replica was obtained. In other processes in which the surface is preserved, either too tedious a procedure is required, unsuited to "mass-production" requirements of industrial laboratories, or replicas of insufficient contrast and sharpness are produced.

In general, investigations with the electron microscope involve five steps: (1) polishing the surface of the metal specimen, (2) proper etching of the surface, (3) preparing the suitable replica from the surface, (4) examination and photography in electron microscope and (5) interpretation.

Preparation of Metal Surfaces

Usual metallographic polishing is generally satisfactory. It is important though that the final polish be applied very carefully, since otherwise evidence of a small amount of deformation might show up even on relatively deeply etched surfaces. A high-power microscope should be used to determine the suitability of the polish and etch. This, of course, is not different from optical examinations, but in these, if a deep etch is used, the problem is less serious.

It is frequently difficult to detect with optical microscopes poor polishing aside from superficial scratches before etching. Figs. 1 and 2 show micrographs of "well" and "poorly" polished nickel etched by immersing the sample for 20 min. in a solution containing 8 grams cupric sulphate in 40 C.C. of concentrated HCl and 40 C.C. of H2O (Marble's reagent). The sample shown in Fig. 1 was polished in its final stages for 5 min. on a carborundum wheel followed by 10 min. on a rouge wheel, whereas the sample shown in Fig. 2 was polished only 1 min. on the rouge wheel. Generally, this procedure does not guarantee that the surface of the specimen will be either undistorted or deformed. It was applied here merely to show the effects of good and poor polishing. To the experienced investigator, plastic deformation is
FIG. 1.—Optical micrograph of well-polished nickel specimen. $\times 1000$.
Fig. 2.—Micrographs of poorly polished nickel specimen. $\times 1000$. 

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visible in Fig. 2. The lamellar etching structure shown in the two bottom grains in Fig. 1 appears fragmented in similar oriented grains in Fig. 2. For comparison, replicas from the surface will become more difficult for deeper etches. Also, if optical microscopes are used to observe the deep etches, the samples may appear there

electron micrographs are shown of the same surface, though not the identical spots, in Figs. 3 and 4, respectively.

After a good polish has been obtained, the next problem is the choice of etchants and etching techniques. As is true also for optical examinations, many etches are not suitable for investigation with the electron microscope; in fact, for the latter the number of suitable etches is more limited. The reason for this lies in the development of a characteristic inner grain structure, which will be discussed in further studies.

Deeper etches will reveal to a better degree the grain and inner grain structures of the metals. Thus it is often advisable to double or even triple the etching times recommended for the various solutions. On the other hand, the separation of the "badly" overetched (Figs. 1 and 2), though in the electron microscope a "nice" structure is visible for the same etch (Figs. 3 and 4).

It is important to remember that the different etching solutions will develop different inner grain structures, since the various alkali or acid etchants differ in their attack upon the various crystallographic planes.

Thus in copper a propionic acid etch tends to produce an octahedral structure (Figs. 5 and 6) attacking the \{111\} planes to a lesser degree than the \{100\} planes. The 50 per cent NH₄OH (20 c.c.) — H₂O₂ (5 c.c.) etch tends to show a cubic block structure (Fig. 7) different from the lamellar cubic structure obtained with the ferric
Fig. 5.—Copper etched with propionic acid (40 c.c.)—H₂O₂ (15 c.c.).
Etching time 20 minutes.

Fig. 6.—Copper etched with propionic acid (40 c.c.)—H₂O₂ (15 c.c.).
Etching time 15 minutes.

Fig. 7.—Copper etched with 50 per cent NH₄OH (20 c.c.)—H₂O₂ (5 c.c.).
Etching time 60 seconds.

Fig. 8.—Copper etched with FeCl₃ (10 grams), alcohol (120 c.c.) and HCl (30 c.c.).
Etching time 40 seconds.
All × 5000.
chloride (10 grams) in alcohol (120 c.c.) and HCl (30 c.c.) etching reagent (Fig. 8).*

“Shadow-casting” Replica Technique

After the sample has been properly polished and etched, a thin, transparent replica is made from the surface of the metal specimen. Best results have been obtained so far with either collodion or formvar films. The first part of the method used here is essentially the same as developed by Schaefer and Harker, of the General Electric Co., and described by the authors in various papers. A replica is prepared by spreading a dilute solution of formvar or collodion in a solvent over the surface of the specimen. As the solvent evaporates a very thin film is formed, which should be thick enough to show the blue or green interference colors (i.e., not more than a few thousand Ångström units). Before the replica is removed from the specimen, a piece of scotch tape, upon which a 200-mesh wire screen has been placed, is then pressed firmly upon the surface of the replica. To protect the center of the wire screen from the glue of the tape, a piece of thin paper (about 2 mm. thick) is inserted between the tape and the screen. To ease the removal of the replica, it is often advisable to breathe heavily upon the specimen, as the moisture in the breath will assist in loosening the film from the metal.

This transparent replica obviously will not possess a great deal of contrast, since, being made of an organic substance, its atoms are too light to absorb or scatter effectively the electrons in the electron beam. For this reason the so-called “shadows” are deposited on the surface of the replica.

The replica is then placed into a vacuum system for deposition of a metallic film upon the impressed surface.* There are many points in the technique that effect the quality of the image. The farther the replica is placed from the filament, the sharper the shadows will be, since then the rays will be more nearly parallel. On the other hand, more metal must be evaporated, as the thickness of the sublimed film will decrease as the square of the distance. For most evaporations an angle of replica surface to line from filament to replica of about 40° to 50° should be used, though if a very fine structure—precipitated particles, for example—is to be observed with shadows, smaller angles should be applied.

It is important that the medium used in the evaporation does not crystallize upon condensation at room temperature. Thus, most metals of high boiling points are suitable. This, of course, varies for the different metallic materials, depending upon the complexity of the crystal structure and the recrystallization point. For face-centered cubic metals, gold with a boiling point of 537°F represents a borderline case. Very thin films will appear structureless, though heavier deposits will give evidence of crystallization. Thus the structure shown in Fig. 9 of a collodion replica of a nickel specimen (same surface

* Covering replicas with a thin film of a suitable metal is not new. For the electron microscope “shadow casting” was first reported by Muller, who applied the technique to measure the height of fine particles. Mahl followed with the evaporation of metallic shadows (chromium) upon surface replicas. In this country the same techniques were reported recently by Thomasson, Williams and Wyckoff. The various authors found that the metal film deposited by evaporation onto the replica will produce shadows of great sharpness, which will show up the surface structure of the specimen in excellent detail. This method in its present development combines most of the advantages of the previous replica techniques. The ease with which replicas may be prepared, and the detail, contrast, and sharpness, will make this “shadow-casting” method an important tool in metallographic investigations with the electron microscope requiring high magnifications and resolving power.
as in Fig. 3, though not the identical area) is due to "granulation" of the gold "shadow." Fig. 8 represents a better specimen.

Fig. 9.—Gold shadow-cast replica of nickel showing crystallization due to too heavy a deposit.

Fig. 10.—Chromium shadow upon a wrinkled collodion replica of nickel.

Both X 5000.

(thinner) gold shadow-cast replica of a copper specimen. Even here a small amount of granulation is visible.

Body-centered cubic chromium has been used with far more success. Figs. 3, 10, and 13 represent chromium shadows.

Manganese (cubic complex, boiling point 3904°F.) has been applied by the author with best success. It produces shadows of great sharpness, and does not show evidence of crystallization even for very heavy deposits. With the exception of Figs. 3, 8, 9, 10 and 13, all electron micrographs in this report are made of manganese "shadow-cast" collodion replicas.

It is important that the replica be supported smoothly by the mesh-wire screen; otherwise the film may wrinkle and upon evaporation a shadow structure similar to that in Fig. 10 may appear. This structure may be interpreted falsely as due to strains on the surface of the original specimen.

Appearance of Shadow-cast Replicas

Two factors determine the difference in blackening on the photographic plate; namely, the thickness of the replica film and the relative thickness of the shadow (thickness parallel to the electron beam).

The former is direct in that the thinner the replica the fewer electrons will be absorbed or scattered. Thus the photographic plate will receive more blackening, producing lighter areas on the print. In other words, "hills" on the original metal surface will appear on the final photographic print lighter than the "valleys."

The second factor may be defined as "the relative thickness of the shadow," and is caused by the metal film formed on the replica. Usually this one is of the greater importance. In "shadow-casting"
areas perpendicular to the path of the atoms emitted from the filament by evaporation will receive the heaviest 

The oxide layer method developed by Mahl\textsuperscript{13} consists essentially of an oxide film produced electrolytically on the sur-

face of the metal. Since mercury does not attack metallic oxides, this film may be removed by immersing the specimen in mercury or mercuric chloride.\textsuperscript{14} When the surface is scratched, the mercury penetrates between the metal and its oxide layer and lifts up the latter. This method has been applied successfully so far only on aluminum, for which very good electron micrographs have been shown by a variety of investigators. Since this method necessitates the destruction of the original surface, it has not been widely accepted.

Another method, also developed by Mahl, has until recently been popular in Germany. In this method, a thin lacquer or collodion film is formed on the surface of the specimen. At first this replica was removed by dissolving the metal.\textsuperscript{9} Since this again required the destruction of 

\[ \text{Comparison of Discussed Technique with Older Replica Methods} \]

The shadow-casting technique was developed in order to overcome many of the disadvantages and shortcomings of the previous methods, which will be discussed in the following paragraphs.

\[ \text{Fig. 11.—Schematic representation of shadow-cast replica.} \]
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FIG. 12.—SHADOW-CAST REPLICA OF PEARLITE.

FIG. 13.—SHADOW-CAST REPLICA OF NICKEL.

Compare etching blocks with micrograph of same sample in Fig. 1.

FIG. 14.—SHADOW-CAST REPLICA OF GRAY CAST IRON.

FIG. 15.—SHADOW-CAST REPLICA OF LOW-CARBON IRON SHOWING CARBIDES AND INNER GRAIN
ETCHING STRUCTURE.

All $\times$ 5000.
the surface, Mahl lately has improved his method by removing the replica electrolytically.\textsuperscript{15}

To show this, the copper sample etched with propionic acid (Figs. 5 and 6) was subjected to the molding process just described. Manganese shadow-cast replicas were then made of the copper surface (Figs. 16 and 17). Deformation and oxidation is clearly recognizable. Since, in addition, this process is on the whole rather tedious, it may lose its present importance.

Good results may also be obtained with the silver-collodion process,\textsuperscript{17,18} which again, besides being rather tedious, lacks the contrast and sharpness obtained with the shadow-casting technique. In this process a silver layer is built up on the surface of the specimen by evaporation in a vacuum. After the layer has been removed from the surface, a collodion film is spread over the silver replica and the latter is then dissolved in weak nitric acid, which does not attack the collodion. The collodion replica is studied in the electron microscope.

The formvar method perfected by Schaefer and Harker\textsuperscript{2-6} consists of forming a formvar or collodion film on the surface of the specimen and removing this film by immersion in water or by various other stripping processes. A lack of sufficiently high contrast and sharpness often make it difficult to interpret electron micrographs prepared by this formvar method.

In this country the polystyrene-silica method of Heidenreich and Pack\textsuperscript{16} has so far been used in most studies, since with it replicas of great sharpness, detail, and contrast are produced. As this method requires a molding process at a temperature of close to 150°C and about 3000 lb. per sq. in. pressure, a small amount of surface deformation and oxidation may appear on many electron micrographs. Unfortunately, previous authors so far have neglected to consider these effects.
CONCLUSION

Comparison of the electron micrographs shown in this report with those obtained by previous authors and shown in the references mentioned shows the advantage of this new "shadow-casting" process. Not only does this method produce replicas of high contrast and sharpness, but the short time required for preparation of the replicas will make this method an easy and quick approach to detailed metallographic investigations.

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