Manual on

ELECTRON METALLOGRAPHY TECHNIQUES

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MANUAL ON ELECTRON METALLOGRAPHY TECHNIQUES

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Committee E-4 on Metallography
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Foreword

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Related ASTM Publications

Applications of Modern Metallographic Techniques,
STP 480 (1970), $17.00 (04-480000-28)

Application of Electron Microfractography to Materials
Research, STP 493 (1971), $8.25 (04-493000-30)

Stereology and Quantitative Metallography, STP 504
(1972), $9.75 (04-504000-28)

Contents

Introduction 1

Chapter 1—Procedures for Standard Replication Techniques for Electron Microscopy 3

- 1.1 Introduction 3
- 1.2 Specimen Preparation for Replication 3
  - 1.2.1 Mounting 3
  - 1.2.2 Polishing 4
  - 1.2.3 Etching 5
- 1.3 Replication 6
  - 1.3.1 Direct Methods 6
  - 1.3.2 Indirect Methods 13
  - 1.3.3 Fracture Replication 15
- 1.4 Summary 17
- References 18

Chapter 2—Extraction Replica Techniques 19

- 2.1 Introduction 19
- 2.2 General Methods 19
  - 2.2.1 Direct Stripped Plastic Extraction Replicas 20
  - 2.2.2 Indirect Stripped Plastic Extraction Replicas 20
  - 2.2.3 Positive Carbon Extraction Replica 21
  - 2.2.4 Direct Carbon Extraction Replica 22
  - 2.2.5 Extraction Replicas Removed by Two Stage Etching 22
  - 2.2.6 Replication of Thin Surface Films 22
  - 2.2.7 Aluminum Oxide Extraction Replica 23
- 2.3 Tables of Extraction Replica Techniques 24
- 2.4 Bibliography 24
- References 24

Chapter 3—Thin Foil Preparation for Transmission Electron Microscopy 29

- 3.1 Introduction 29
- 3.2 Bulk Thinning to 500 μm (0.5 mm) 29
  - 3.2.1 Cutoff Wheel 29
  - 3.2.2 Spark Machining 30
  - 3.2.3 Electrolytic Acid Saw and Acid Planing Wheel 30
- 3.3 Prethinning to 50 μm (0.05 mm) 30
  - 3.3.1 Surface Grinding and Hand Grinding 30
  - 3.3.2 Cold Rolling 31
  - 3.3.3 Chemical Prethinning 31
  - 3.3.4 Electrolytic and Jet Prethinning 31

3.4 Final Thinning to Less Than 0.5 μm 31
  3.4.1 Bollmann Method 31
  3.4.2 Window Method 32
  3.4.3 Disa Electropol Polishing 33
  3.4.4 Chemical Polishing 33
  3.4.5 Electrolytic and Automatic Jet Polishing 33
3.5 Unique Thinning Techniques 34
  3.5.1 Small Diameter Wires 34
  3.5.2 Microtomy 34
  3.5.3 Ion Micro Milling 34
3.6 General Precautions 35
  3.6.1 Mixing Electrolytes 35
  3.6.2 Polishing Film and Staining 35
  3.6.3 Electrolyte and Specimen Temperature 35
  3.6.4 Cutting and Mounting 36
3.7 Summary 36
3.8 Acknowledgments 37
Appendix 3.1 37
Appendix 3.2 37
References 39

Chapter 4—Selected Area Electron Diffraction Analysis of Extraction Replica and Thin Foil Specimens in the Transmission Electron Microscope 41

4.1 Introduction 41
Part I—Particle or Second Phase Identification Using Extraction Replica and Selected Area Electron Diffraction 42
4.2 Introduction 42
4.3 Technique for Preparing Extraction Replicas 42
4.4 Indexing Selected Area Electron Diffraction Patterns 43
  4.4.1 Calibration of the Microscope Constant 43
  4.4.2 Identification of Unknown Diffraction Patterns 45
  4.4.3 Indexing Simple Single Particle Spot Patterns 45
4.5 Summary 50
Part II—Analysis of Crystallographic Features and Defects in Thin Foil Specimens 51
4.6 Introduction 51
4.7 Steps in the Solution of a Selected Area Spot Electron Diffraction Pattern of a Thin Foil Specimen 52
Appendix 4.1 60
Appendix 4.2 61
Appendix 4.3 62
Appendix 4.4 68
References 72

Introduction

A few years ago subcommittee E04.11 on Electron Microscopy and Diffraction of ASTM Committee E-4 on Metallography initiated a project of preparing recommended procedures for experimental techniques relating to electron metallography. It was intended to provide a concise but practical manual of "how-to" for a nonbiological laboratory involved in various disciplines relating to electron metallography. To accomplish this objective, four task groups were formed.

This special technical publication is a culmination of efforts not only of the members of the task groups and the subcommittee but numerous other contributors. The procedures are written to provide an elementary approach and are intended to be an aid to laboratory personnel with a limited background or expertise in electron metallography. Even though the manual is addressed to a novice, it is believed that some of the material including the exhaustive bibliography appended to each procedure will prove equally useful to those whose interest lie beyond the basic.

The last few years have seen an increased number of publications and textbooks on this and similar subjects. It was felt, however, that all these assumed a certain educational and experimental background on part of the readers. This manual, we believe, fulfills the need in that it is addressed to someone who is just starting out in this field. Therefore, we hope that this special technical publication will not be just an addition to a long list of literature available on the subject but will find its rightful place as a practical manual for years to come.

The list of contributors is acknowledged in the beginning of each chapter. We would like to express our gratitude to B. R. Banerjee and G. E. Pellissier, the past chairmen of the subcommittee, under whose leadership the project was initiated and flourished. Our sincere appreciation to the many contributors for letting us use their "in-house" techniques; and to ASTM for supporting the project and publication of this manual.

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Chapter 1—Procedures for Standard Replication Techniques for Electron Microscopy

1.1 **Introduction**

While substantially supplemented in the last decade by thin foil transmission and scanning electron microscopy, replica electron microscopy remains a major technique in contemporary metallurgical investigations.

The best attainable resolution with replica methods being limited by the replicating material is approximately 20 Å, intermediate between thin foil (approximately 1 Å on 1000 kV units) and scanning electron microscopy (approximately 75 Å on current models) where maximum resolution is governed by the instrument itself.

Time for preparation of specimens for replication is considerably less than that required for preparation of thin foil specimens, and greater than the time required for scanning electron microscopy, where little or no special specimen preparation techniques are required.

The successful use of any replication procedure will normally require a certain amount of trial and error on the part of the investigator. Therefore, this review will summarize briefly the most commonly used methods of replication and emphasize the variations in each step that have been found to affect ease of replication and replica quality.

1.2 **Specimen Preparation for Replication**

1.2.1 *Mounting*

Two factors are particularly important in selection of a mounting material, when required.

A. Resistance of a mounting material against attack by electropolishing solutions, etchants, or replication solutions to which the specimen will be exposed.

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[1] **Prepared by D. A. Nail, Cameron Iron Works, Inc.**

Roughening of the polished surface of the mounting medium through chemical attack can make certain replication techniques, for example, those involving dry stripping, difficult or impossible. Certain "cold mount" compounds, for example, are susceptible to attack by some solvents used in replication, hence poorly suited for replica electron microscopy.

Where experience or information on the suitability of the mounting material for a specific specimen preparation and replication technique is unavailable, it is frequently advisable to undertake a "dry run" with a mounting compound, exposing the mount to all intended chemicals before mounting the specimens intended for replication.

B. Minimum mold shrinkage around the specimen.

Moderate shrinkage may result in "bleeding" of polishing compounds or etch products from the mold-specimen interface, which may create artifacts on the final replicas. Extensive mold shrinkage can cause tearing of replicas at the mold specimen interface in dry stripping techniques. Naturally, standard metallographic precautions in specimen mounting, for example, avoidance of temperatures or pressures which could cause microstructural alterations, should be observed.

1.2.2 *Polishing*

Any of the standard metallographic polishing practices [mechanical, electrolytic, chemical, and polish attack (simultaneous mechanical and chemical polishing)] may be used in preparing specimens for replication. The selection of a polishing method is dictated by the alloy to be studied, as is the case in light microscopy. Detailed discussions of the various methods are given elsewhere and will not be included here.

1.2.2.1 *Mechanical Polishing*—Two major objectives in mechanical polishing for replica electron microscopy are:

A. Removal of all traces of smeared or "disturbed" metal to ensure that the structural features observed on the final replica are genuine and not artifacts.

B. Production of a scratch free surface as possible for subsequent replication. It should be noted that specimens which appear to be virtually scratch free on the light microscope may appear badly scratched during the examination in the electron microscope. This is due to the enhanced contrast imparted to surface features during later shadowing of the replica, as well as to the greater resolution of surface features obtained in the electron microscope.

To ensure as nearly a scratch free surface as possible, it is essential that specimens be washed, preferably ultrasonically, between each grinding and polishing step. Where diamond polishing is used, selection of a suitable solvent—xylene, varsol, etc.—for removal of the suspension medium for the diamond particles is important.

It should be noted that many investigators have found vibratory polishing which incorporates a significant vertical component to the vibratory motion to be highly useful in the examination of certain alloys. The enhanced relief imparted to minor, for example, grain boundary, microconstituents may permit general examination of the microstructure in the unetched condition on the light microscope and should require lighter than normal etching for later production of sharp, high contrast replicas.

1.2.2.2 *Electrolytic Polishing*– The major concerns with electropolishing of specimens for replica electron microscopy are:

A. Removal of all traces of the electrolyte prior to replication, through washing in appropriate solvents.

B. Awareness of any selective attack. As many alloys contain microconstituents which may be either cathodic or anodic with respect to the alloy matrix, certain microconstituents may be either severely attacked or relatively unattacked during the electrolytic polishing procedure, resulting in pitting and misleading morphological characteristics or extensive particle relief. Such selective response may be desirable for specific applications, for example, in distinguishing between two different known constituents of similar morphology but different electropotentials. It is imperative, however, that the investigator be aware of the nature of any such selective attack.

1.2.2.3 *Chemical Polishing and Polish Attack*–The precautions necessary for replica electron microscopy are similar to those of the methods previously discussed, for example, (1) complete removal of any traces of chemicals employed in polishing and (2) avoidance or awareness of the nature of any selective microconstituent attack occurring during polishing.

1.2.3 *Etching*

Three areas in the etching process are particularly significant in replica electron microscopy:

A. Any traces of etchant or etch products must be removed from the specimen surface before replication, as such a residue may lead to errors in structural interpretation through obscuring microconstituents, altering their apparent morphology or being confused with actual microconstituents.

B. Selective attack by the etchant(s) employed on specific microconstituents should be avoided unless the nature of the selective attack is clearly recognized; in some cases, selective attack may be used as a means of distinguishing between morphologically similar constituents.

C. With the notable exception of extraction replication, etching time for replica microscopy is shorter than that employed in light microscopy. Heavy etching commonly tends to disfigure particle morphology through attack at particle-matrix interfaces, rendering structural interpretation more difficult.

The specific etching technique used by the investigator–usually chemical, standard electrolytic, potentiostatic, or ion bombardment–will typically require a certain amount of trial and error in the first few applications, in order to determine the ideal depth of etching for a particular alloy and minimize problems such as those just discussed.

1.3 Replication

Two general classes of replication are commonly used in metallurgical investigations:

A. Direct or single-stage methods, in which a replica is made of the specimen surface and subsequently examined in the electron microscope.

B. Indirect methods, that is, multistage, in which the final replica is taken from an earlier primary replica of the specimen surface.

Both approaches have advantages and disadvantages in terms of resolution, freedom from artifacts, time of preparation, etc.

Selection of a particular replicating technique is made on the basis of the information desired from the investigation, the suitability of the method for the alloy of interest, and specimen configuration and size.

The resolution of all replica methods is dependent primarily on the structure of the replicating material and will be discussed separately with each method.

1.3.1 *Direct Methods*

The most extensively used direct methods involve either plastic, carbon, silicon oxide, or aluminum oxide (aluminum alloys only) as the replica material.

All direct methods except plastic methods are destructive, requiring repreparation of the specimen before making additional replicas.

This discussion will restrict itself to the most widely used of these methods, plastic and direct carbon replication; silicon oxide replication is almost identical to direct carbon replication, and both silicon oxide [*1-3*][2] and aluminum oxide [*2-4*] replication techniques are extensively described in reference literature.

1.3.1.1 *Plastic Replicas* [1-3,5]—While resolution with plastic methods is limited to approximately 200 Å, these methods are used occasionally for low magnification work because of their relative simplicity and short preparation time. The most commonly used plastics are:

Collodion—Cellulose nitrate, typically 0.5 to 4 percent in three parts ethyl ether and one part ethanol or in amyl acetate.

Parlodion—Cellulose nitrate, typically 0.5 to 4 percent in butyl acetate.

Formvar—Polyvinyl formal or polyvinyl acetal resin, typically 1 to 2 percent in dioxane or 1,2 dichloroethane (ethylene dichloride).

1.3.1.1.1 *Application of plastic*—A few drops of the plastic solution are applied to the surface to be replicated, usually from a dropping bottle, and allowed to dry.

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[2] The italic numbers in brackets refer to the list of references appended to this chapter.

The specimen is tilted usually at 90 deg to the horizontal during drying to promote a thinner replica.

Since resolution increases with thinner replicas, while ease of replica stripping increases with thicker replicas, some trial and error in terms of plastic concentration may be necessary during the first few attempts in order to strike a balance between resolution and successful replica stripping.

After drying, the replica can be stripped from the specimen surface by two methods.

1.3.1.1.2 *Dry stripping*–(Fig. 1) is the simpler and faster of the two stripping methods, although occasional structural distortion can be induced in the replica with this method.

In dry stripping, one or more circles or squares of thin paper (usually lens tissue), slightly smaller in diameter than the electron microscope specimen grid

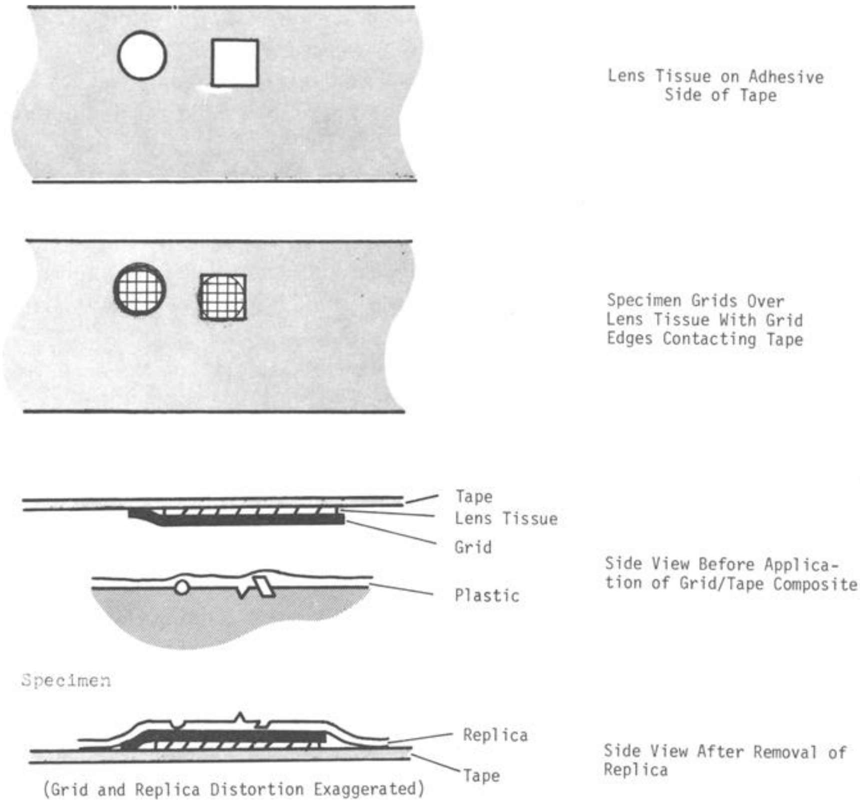

FIG. 1–*Schematic illustration of dry stripping.*

(usually 2.7 or 3 mm diameter), are pressed against the adhesive surface of a piece of cellulose tape. A specimen grid is then placed over the paper so that only the periphery of the grid is held by the tape. By using a 3 mil thick grid, it may not be necessary to use the thin paper as a separator between the grid and the tape.

The replica is then moistened slightly by breathing on it, and the tape, with paper and grid face downward, is pressed rather firmly against the moistened replica.

After the replica has hardened again, typically 10 to 20 s, the tape is stripped carefully from the specimen with replica, grids, and paper adhering to the tape.

If the replica tears around the grids during stripping, this may be remedied by:

(*a*) More gentle stripping (more acute angle between tape and specimen surface, and slower stripping).

(*b*) Thicker replica (more concentrated solution or more nearly horizontal drying, with the former preferred, since the latter may exaggerate any varying replica thickness from top to bottom edge of the specimen).

(*c*) Stripping sooner after the tape has been pressed on the replica (the moister replica will strip more easily but is also more subject to distortion during stripping).

At this stage, the replica may be shadowed for higher contrast. Shadowing techniques are discussed subsequently in connection with direct carbon replication.

After stripping, the grid and replica are carefully removed from the tape, usually by cutting around the edge of the grid with a scalpel and lifting the grid and replica free from the tape and paper with tweezers.

The replica is then placed in the electron microscope specimen holder for examination.

1.3.1.1.3 *Wet stripping* is commonly used where the replica cannot be removed by dry stripping. While more reliable than dry stripping, in that distortion of the replica during stripping is minimized, it is considerably more time consuming.

A 1 percent solution of formvar is applied to the specimen surface and allowed to dry.

A heavy backing film (typically 5 percent collodion in amyl acetate) is applied over the dry formvar replica and allowed to dry horizontally. One to two drops are generally sufficient, depending on specimen size.

The composite films are removed from the specimen by lowering the specimen face up into a dish of distilled water at a shallow (10 deg or less) angle. The composite is "teased" free from the specimen surface with a needle, with the surface tension of the water causing the replica to float on the surface as it is freed.

The composite replica may be shadowed after being freed for increased contrast.

The collodion backing can then be dissolved by placing several electron microscope specimen grids on a piece of fine (100 mesh) copper gauze, removing any remaining water with filter paper, placing the collodion-formvar composite over the grids and gauze, and dissolving the collodion backing by passing a slow stream of amyl acetate from a burette over the gauze for approximately 15 min.

The grids and formvar replicas are then cut away from the unsupported formvar and mounted in specimen holders.

The negative replica obtained is illustrated in Fig. 2.

1.3.1.2 *Direct Carbon Replication* [1-3,5] –While both carbon and silicon oxide yield relatively stable and finely structured replicas with a resolution approaching 20 Å, the carbon replica is more widely used, primarily because of its easier evaporation and greater visibility after evaporation.

Both of these techniques destroy the surface to be replicated, necessitating repreparation of the specimen before making additional replicas.

The first step in preparation of direct carbon replicas is vacuum deposition of carbon onto the polished and etched specimen surface. (Alternatively the specimen may be shadowed after carbon deposition, as described subsequently.)

A typical vacuum deposition setup is shown in Fig. 3.

A moderately high vacuum (5×10^{-4} torr min) is necessary to ensure an essentially structureless, high resolution replica. While the amount of carbon evaporated varies somewhat, a 10-mm-length of 1-mm-diameter carbon rod is typical (Fig. 3, detail *A*).

A final replica thickness of 100 to 200 Å is optimal in most work. The thickness of the evaporated carbon replica is important, since thicker replicas tend to curl during later separation and washing, while thinner replicas are more prone to break up.

Thickness of the evaporated carbon can be roughly estimated by putting a drop of clear oil on a small porcelain plate and placing the plate next to the specimen in the evaporator. As carbon is deposited, the porcelain plate will darken with the exception of the spot covered by oil; when the plate is light grey in color, the carbon film thickness is roughly 200 Å. Alternatively, the film thickness may be determined by optical density measurements.

1.3.1.2.1 *Shadowing* [1-3,5,6] –As the carbon replica is rather low in contrast, the replica is usually shadowed in order to improve the contrast of the final replica.

Shadowing consists of vacuum evaporation of a high melting point element–typically platinum, palladium, chromium, or germanium–at a predetermined angle to the specimen surface. The shadowing material is typically held in a tungsten boat or coil (Fig. 3, detail *B*).

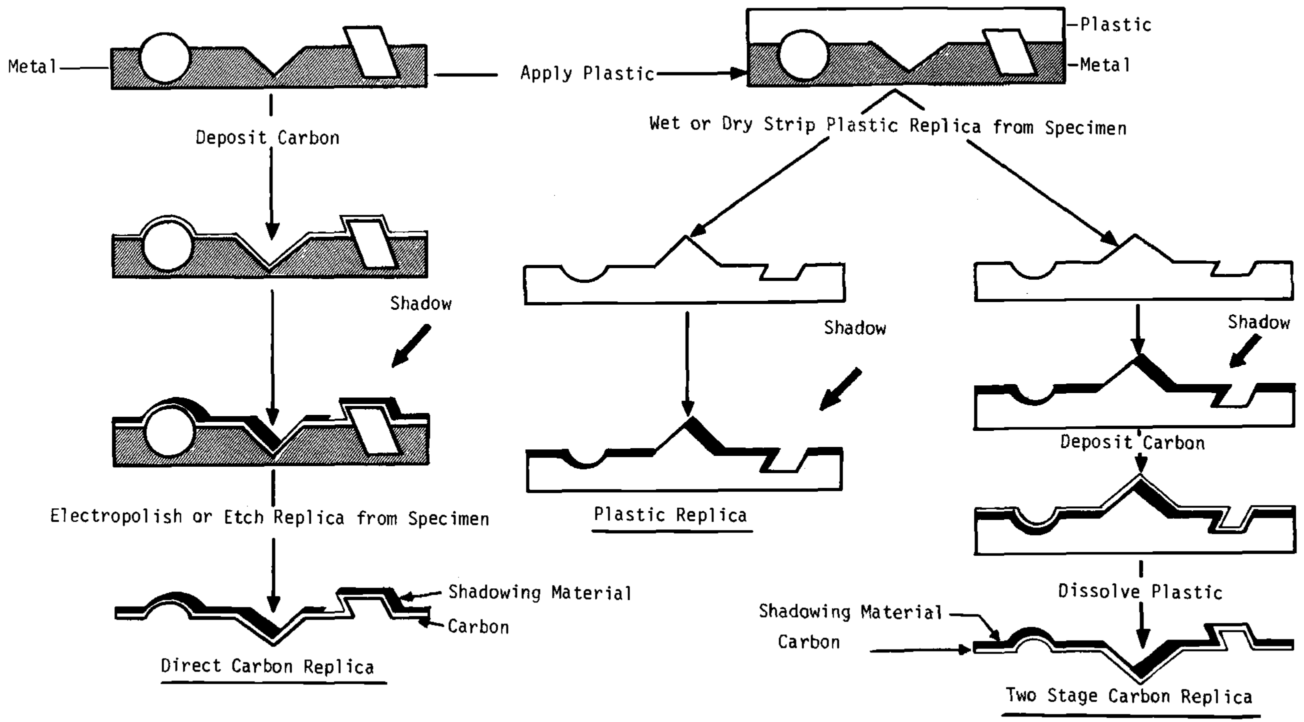

FIG. 2—*Schematic representation of three replication techniques.*

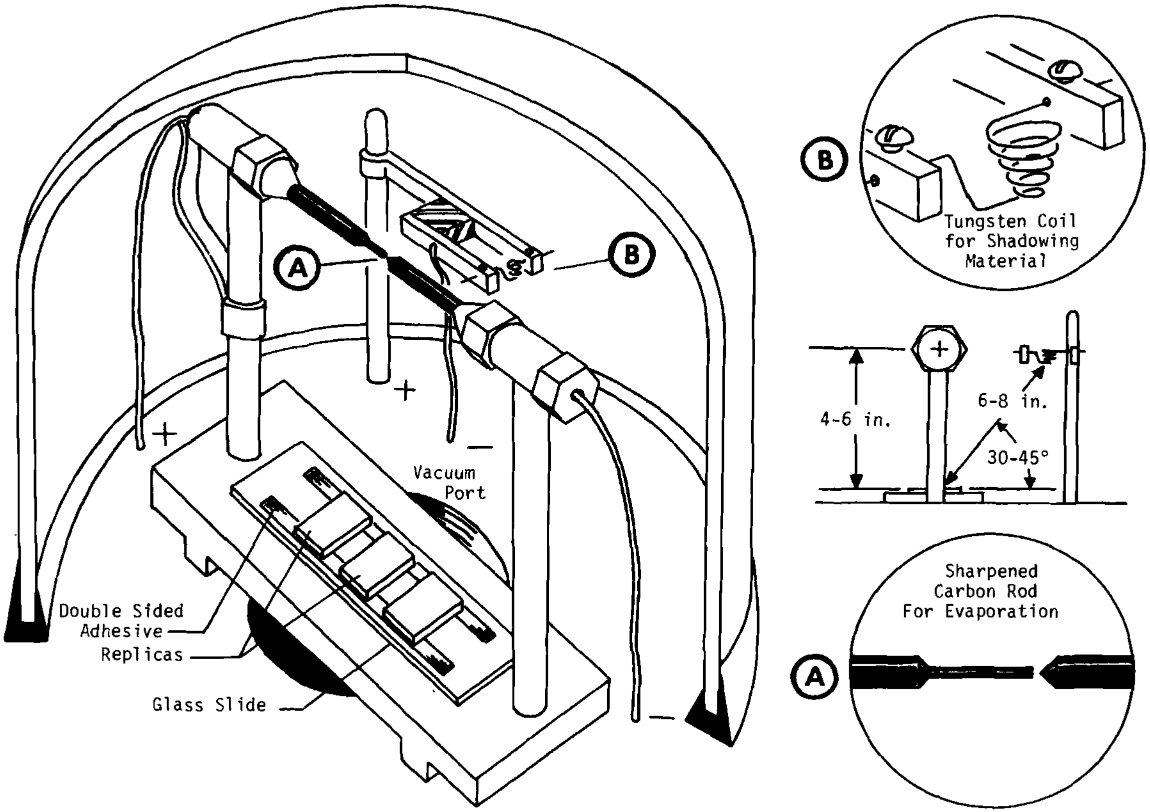

FIG. 3—*Typical vacuum deposition setup.*

Selection of the shadowing material is based primarily on resolution requirements, with higher melting point elements such as platinum being more suitable for higher resolution replicas because of their generally finer crystallite size after vacuum deposition.

Platinum/carbon shadowing—Platinum/carbon shadowing provides the highest resolution among shadowing methods commonly used.

In this method, platinum and carbon are evaporated simultaneously from: (*a*) special rods consisting of an inner core of platinum with an outer layer of carbon; or (*b*) pellets consisting of approximately 50 percent carbon, 50 percent platinum with the platinum in the form of fine particles in the carbon matrix.

The rods or pellets are evaporated in the manner described earlier for carbon evaporation, usually with the addition of a large screen with a small aperture to limit platinum-carbon deposition to the vicinity of the specimen and reduce contamination of the vacuum deposition apparatus.

Shadowing angle—The shadowing angle is usually 30 to 45 deg to the specimen surface with a 6 to 8 in. separation between the shadowing source and the specimen. Selection of the shadowing angle is based primarily on etching depth of the specimen and size of the microconstituents of interest; very lightly etched specimens are shadowed at more acute angles (as low as 15 deg), and more heavily etched specimens shadowed at higher angles. Likewise, finer particles or grain boundary constituents are better discerned by low angle shadowing.

1.3.1.2.2 *Separation of replica from specimen*—After removal from the vacuum chamber, the replica is scored around the edges of the specimen and is typically scribed into approximately 3 mm squares.

The shadowed replica is then removed by either chemically etching or electropolishing the specimen until the replica floats free. Electropolishing is normally favored over chemical etching, since the heavy etching necessary to free the replica promotes retention of minor microconstituents in the replica (extraction replication is discussed in Chapter 2).

If difficulties are encountered in separation of the replica from the specimen surface—for example, partial disintegration of the carbon replica during separation, incomplete separation of the replica from the specimen, etc.—several approaches can be used to facilitate easier replica separation:

(*a*) A thicker carbon film may be deposited to reduce replica fragmentation.

(*b*) The separation technique, for example, etchant or electrolyte composition, current density during electropolishing, etc., may be altered.

(*c*) Shadowing and carbon deposition may be preceded by vacuum deposition of a wetting agent on the specimen surface. The wetting agent, usually boron oxide[*3*], or Victawet[*6*], is vacuum deposited prior to carbon or shadowing material and is reported as greatly facilitating replica separation as well as contributing to cleaner replicas.

After separation, the replicas are picked up on 200 mesh specimen grids, washed in two or more baths of distilled water, and transferred on specimen grids to filter paper to dry.

After drying, they are ready for examination in the electron microscope. This technique is illustrated schematically in Fig. 2.

1.3.2 *Indirect Methods*

While limited by certain inherent disadvantages, two stage carbon replication methods[*1,3,5*] are used very widely.

The major advantages include:

A. High resolution (approaching 20 Å under ideal conditions).

B. Retention of the specimen surface condition for additional replication without specimen repreparation.

C. Suitability for specimens for which direct carbon replication is difficult or impossible.

Some of the disadvantages are:

A. Somewhat less clean replicas than direct carbon replicas (partly because of the difficulty of removing the last traces of the plastic primary replica from the carbon film).

B. Occasional artifacts[*8*] if the technique is not skillfully employed.

The general procedure involves: (1) preparation of an initial plastic replica, which is sometimes backed with a secondary plastic for strength during stripping[*9*]; (2) shadowing and carbon deposition of the plastic primary replica; and (3) dissolution of the plastic replica[*10*], leaving the shadowed carbon replica for examination in the electron microscope. This procedure is illustrated schematically in Fig. 2.

Two examples will be reviewed as an introduction to the two-stage technique. It should be kept in mind that numerous variations of these and other techniques are being used quite successfully, and that successful replication will depend largely on careful laboratory practice and "trial and error" experience on the part of the investigator in applying these techniques.

1.3.2.1 *Nitrocellulose Primary Replicas*—A few drops of a 2 to 3 percent solution of nitrocellulose in amyl acetate are poured on the specimen surface, and the specimen is tilted to allow the plastic to dry vertically, as described earlier. The replica is dry stripped with adhesive tape pressed directly against the plastic replica, and shadowing material and carbon are deposited as described previously. The tape and replicas are then cut into 3 to 5 mm squares and placed carbon side up in a petri dish.

A small amount of petroleum ether is added to the petri dish to dissolve the gum on the tape. Fifteen to thirty minutes are typically required for dissolution of the adhesive gum, after which the nitrocellulose-carbon replica is separated from the tape, usually with needle and tweezers, and placed in a second petroleum ether bath to dissolve any remaining tape gum.

The replica is then picked up on a microscope grid with the carbon side down and transferred to dry filter paper. The filter paper is wet thoroughly with amyl acetate: Two to four baths are usually required to dissolve the last traces of nitrocellulose, with the first bath usually left overnight and the subsequent baths of 1 to 3 h duration.

If the replicas are needed quickly, amyl acetate may be dropped directly onto the replicas from a burette as described earlier.

After washing, the specimens are ready for examination in the electron microscope. A variation of this technique not requiring the petroleum ether intermediate soak is also rather widely used.

A collodion replica is dry stripped with microscope grid and thin paper between the replica and the tape as described earlier.

After carbon deposition and shadowing, the collodion-carbon replica and grids are separated from the tape and paper.

The simplest separation procedure involves tilting the glass slide on which the replicas are mounted at a slight angle (typically 10 to 15 deg) to the horizontal, and dropping one or two drops of amyl acetate just above the replicas. The amyl acetate dissolves most of the collodion, making it relatively simple to cut around the specimen grid with a scalpel or needle, lift the grid and replica from the paper and tape, and wash the replica in amyl acetate to dissolve the remaining collodion as described earlier.

1.3.2.2 *Cellulose Triacetate Primary Replicas*—A thin sheet (as thin as 0.0005 in. for lightly etched surfaces) of cellulose triacetate (bexfilm or faxfilm) is immersed in acetone for a few seconds and pressed lightly over the specimen surface.

After the sheet has dried (typically 5 to 10 min), the sheet is dry stripped, mounted replica face up on a glass slide, and placed in a vacuum evaporator.

After shadowing and carbon evaporation, the replica is removed from the evaporator, and the carbon side of the replica is lightly coated with petroleum jelly. The petroleum jelly reduces the tendency of the carbon replica to disintegrate after dissolution of the plastic.

The replica is then cut into 2 to 4 mm squares and immersed in a covered dish of acetone for several hours, typically overnight, until the plastic primary replica is completely dissolved.

The carbon replicas are picked up on copper specimen grids and transferred to a carbon tetrachloride bath for about 3 h to dissolve the petroleum jelly.

The replicas are then transferred on copper grids to a distilled water bath, typically with alcohol and 50-50 water-alcohol as brief intermediate baths before transferral to the water bath. The final water bath tends to flatten any replicas which have curled during the earlier baths.

Finally, the replicas are picked up on clean copper grids, which are normally dipped in alcohol first, and placed on clean filter paper to dry. The replicas are then ready for examination in the electron microscope.

1.3.3 *Fracture Replication*[11-15]

Replication of fracture surfaces is quite similar to replication of polished and etched microspecimens.

The major differences are in specimen preparation, which is usually minimal for fracture surfaces, and the mechanics of removing a replica from the comparatively rough fracture surface.

1.3.3.1 *Specimen Preparation*—Specimen preparation before replication is comparatively simple, and is largely dictated by the necessity to avoid damage or contamination of the fracture surface.

As a clean fracture surface is essential to correct fractographic interpretation, the investigator should avoid handling the fracture surface, as any contamination from human hands will stain and obscure fractographic features.

Joining of mating fractures should be avoided, since some scoring of fracture features is unavoidable in this process.

Ideally, the fracture surface should be protected from general atmospheric or chemical attack by sealing in a plastic bag or coating with a suitable plastic (any of the standard replicating plastics will usually do) until the fracture is replicated.

As some contamination is frequently present on the fracture surface from earlier handling by nonlaboratory personnel, the fracture must be cleaned before replication. While the specific cleaning procedure will vary with the alloy composition and the nature of the contamination, if known, ultrasonic cleaning in a suitable solvent such as acetone, trichloroethylene, etc., is widely used to remove oil and grease.

Removal of oxides or other chemical reaction products is more difficult and only marginally effective, as fracture features have been already altered by chemical reaction with the base metal and cannot be restored to their original condition.

1.3.3.2 *Replication*—The most commonly used fracture replication techniques are direct carbon replication and two stage carbon replication.

Other methods, for example, polystryene pellet replication[*11*] and lucite replication[*16*], are also used but will not be described here.

1.3.3.2.1 *Direct carbon fracture replicas*—While offering the highest resolution of the fracture replica techniques, direct carbon replication is usually limited to fracture surfaces which can be safely destroyed, since this method modifies the fracture surface beyond useful further replication.

After cleaning, the fracture is placed in a vacuum evaporator, fracture face up. If only a selected area of the fracture is of interest, the remainder of the fracture may be masked off with an appropriate lacquer.

Carbon is evaporated first and followed by shadowing as described previously. The fracture is commonly oriented in the vacuum evaporator so that shadowing direction corresponds with macroscopic fracture direction.

After removal from the vacuum evaporator, the fracture and replica are normally scored into 3 to 5 mm squares to promote easier separation of the replica and fracture.

The replica is separated from the fracture by electropolishing or chemical etching; the etching will permit the retention of minor constituents in the replica.

Some experimentation is usually necessary to determine optimum replica separation techniques for particular alloys, for example, in terms of current density, electrolyte or etchant composition, to minimize replica breakup in this step.

After separation from the fracture surface, the replica is picked up on fine (typically 200 mesh) screen and transferred to the first washing bath, usually distilled water.

Surface tension reducers, such as zephiran chloride, are often added in small amounts to the water bath to minimize replica motion and simplify pickup with the fine screen.

Severely curled replicas may be straightened by being transferred briefly to an ethyl alcohol bath and back to a fresh water bath, or by addition of a few drops of commercial carbon film straightener to a second water bath.

Finally, the replicas are picked up on clean electron microscope specimen grids and placed on fresh, covered filter paper, replica side up, to dry. Once dry, they are ready for examination.

1.3.3.2.2 *Two stage carbon fracture replicas*—This method is similar to the one used for examination of microspecimens. The two stage technique offers the advantage of not destroying the replicated surface. This is often of major importance when the fracture represents a condition not easily duplicated, for example, service failures or long time tests.

The major disadvantages of the two stage technique are its somewhat longer preparation time, its somewhat reduced resolution, and the increased possibility of artifacts.

The latter is of special importance in fracture replicas, with the comparatively rough fracture topography being somewhat difficult to replicate faithfully because of occasional incomplete plastic flow over the rugged, varied fracture facets.

The plastic medium most commonly used in replicating fractures is cellulose acetate tape, usually one to five mils in thickness. In general, the thinner the tape the better, since thicker tapes will accentuate the tendency of deposited carbon to disintegrate during later dissolution of the plastic. (Cellulose acetate swells by approximately 50 percent during dissolution in acetone, subjecting the carbon film to considerable strain; the effect on the carbon film is of course greater with thicker tapes.)

The tape is wetted on one side by a few drops of acetone, held a few seconds until the tape assumes a milky color, and pressed firmly, wet side down, onto the fracture surface.

The tape is held against the fracture surface for 1 to 2 min until partially dry, and then left to dry completely (usually about 10 min). The tape is then dry stripped from the fracture.

If the tape tears during stripping, thicker tape is usually necessary.

For extremely rough fractures, a two step plastic application may be necessary.

A strip of tape is dissolved in acetone, and the solution is poured over the fracture surface. A dry strip of relatively thick (3 to 5 mils) tape is then pressed on the still wet plastic solution and held in place until almost dry (typically 3 to 5 min). After drying, the combined replica is stripped.

The replica is mounted on a glass slide, shadowed (usually in the macroscopic fracture direction) at about 45 deg (lower angles for smoother fractures), and carbon is deposited.

After removal from the evaporator, the cellulose acetate backing is dissolved in acetone.

To reduce distortion or fragmentation on the carbon replica during this stage, several procedures may be used:

(*a*) The plastic-carbon replica may be soaked in a solution of 50 percent acetone, 50 percent ethanol or distilled water, and then transferred to a 100 percent acetone bath.

(*b*) The replica composite can be cut into smaller pieces somewhat larger than the electron microscope specimen grid before immersion in acetone.

(*c*) The replica composite may be soaked in warm acetone.

(*d*) The replica composite may be exposed to acetone vapors for a few hours prior to immersion in a final acetone bath.

(*e*) A specimen grid may be placed on the fracture surface prior to application of the replicating plastic. The grid embedded in the plastic replica restricts its expansion during later dissolution in acetone.

After complete dissolution of the cellulose acetate backing, the replica is ready for examination in the electron microscope.

1.4 Summary

Several rather specialized techniques (for example, successive replication of the same area of a specimen[*17,18*]) are not reviewed in this procedure, but many special techniques are described in Refs *1* and *3*.

It must be emphasized that successful utilization of any replication technique will normally require some trial and error experimentation and patience on the part of the investigator and occasional modification of the replication procedure used.

A modest amount of experience with replication, however, should enable the investigator to utilize any appropriate technique for his investigation with a high degree of success.

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Chapter 2—Extraction Replica Techniques

2.1 Introduction

Small particles such as precipitates and included material in the matrix (such as inclusions) can be examined for shape, size, and distribution using the electron microscope. Thin surface films can also be examined. Using selected area electron diffraction, the particles or films can be identified if they are crystalline in form. Amorphous materials can not be identified by this technique because of diffuse and indistinct diffraction rings.

Techniques for removal of particles from the matrix material or thin films from the surface must be utilized prior to examination by electron microscope. Such extraction techniques can also be used to obtain specimens for examination by conventional electron diffraction, X-ray diffraction, microprobe analysis, etc.

The state of the art of preparing extraction replicas is to the point that the methods and techniques can be classified in a general manner. However, each metal, alloy, or material to be studied has its own characteristics of etching, etc., which cannot be categorized. Thus, some phases of the methods and techniques can be generalized, but skill and experimentation must be employed by the investigator to achieve the desired results.

The purpose of this brief description of extraction replica techniques is to familiarize the new investigator with extraction replica microscopy. It is hoped that this document will serve as an information source for most of the varying techniques used.

2.2 General Methods

In order to extract particles from a specimen, the usual metallographic techniques for micropolishing the specimen are employed. At this point, it should be emphasized that care should be taken to avoid embedding the polishing abrasive into the matrix of the specimen. Such abrasives can become

[1] Prepared by A. R. Marder, Bethlehem Steel Corp.; J. C. Wilkins, Armco Steel Corp.; G. N. Maniar, Carpenter Technology Corp.; D. A. Nail, Cameron Iron Works, Inc.; and D. L. Robinson, Aluminum Company of America.

easily lodged in crevices or porous areas. Careful polishing and the use of polishing abrasive which do not relate in any way to the particles to be studied can minimize this possibility of contamination. Electropolishing can often be employed on many materials in order to avoid this problem.

The polished surface is then etched by a suitable reagent which will attack the matrix, generally leaving particles loose and in relief on the surface.

There are several procedures for making an extraction replica of the particles on an etched surface.

2.1 *Direct Stripped Plastic Extraction Replicas*

This is the simplest extraction replica procedure and in many cases, is quite satisfactory. This method consists of placing a few drops of a dilute solution of plastic on the surface to be replicated and draining off excess solution by standing the specimen on edge. When the excess solution has drained off and the solvent has evaporated leaving a thin plastic coating, the replica is ready for stripping. A 200 mesh (1/8 in. diameter) specimen screen is caught up on a piece of cellophane adhesive tape; the specimen is moistened by breathing on it, after which the tape and screen are pressed firmly onto the specimen surface and immediately pulled off by stripping across the specimen. If a replica is removed, it is easily seen, both by the completeness of removal of the plastic film from the specimen and by the appearance of the screen itself. Usually the plastic film on the specimen screen is discernible by the interference color pattern from reflected light. Often a replica may come off completely where it is in contact with the cellophane tape but not on the microscope grid. Several attempts may be necessary before one or more whole replicas are obtained. Common plastics used in this method are parlodion (pyroxylin, cellulose nitrate–1 to 2 percent solution in amyl- or butylacetate), formvar (polyvinyl formal or polyvinyl acetal resin–1 to 2 percent solution in dioxane), and collodion (pyroxylin, cellulose nitrate–4 percent solution in three parts ethyl ether and one part ethanol).

2.2.2 *Indirect Stripped Plastic Extraction Replicas*

When replica films cannot be removed by the direct "scotch tape" method just described, a plastic replica can be secured usually by using a backing material to give the necessary strength needed for stripping. This backing material is usually another plastic which can be separated from the replica plastic by dissolving in a solvent which does not affect the replica. Some of these are:

A. *Polyvinyl Alcohol* (*PVA*)–This is soluble in water. A 15 percent solution, quite syrupy in consistency, can be applied over the dried replica film 1 percent parlodion. When dry, an edge is loosened with a knife, and the film pulled off. The composite replica is cut into 1/8 in. squares and floated PVA film down in a dish of distilled water. When the PVA is dissolved away, the parlodion squares are fished out onto specimen screens.

B. *Cellulose Acetate Tape*—Formvar is used for the replica, as in the direct stripped procedure. When dry, the specimen coated with formvar is wet with acetone, and a piece of faxfilm tape is pressed on. To facilitate smoothing out, the back of the faxfilm may be wet with acetone and rubbed to ensure good contact. When dry, the faxfilm is stripped from the specimen carrying the formvar film with it. The replica is then cut up into 1/8 in. squares which are placed on specimen screens, and the acetate dissolved away in acetone.

2.2.3 *Positive Carbon Extraction Replica*

A method for securing extraction replicas of metal specimens that has been found quite satisfactory is the positive carbon replica, sometimes called a metal replica. The steps involved in positive carbon extraction replication are as follows:

A. The surface to be replicated is wet with one or two drops of *p*-dioxane, and a small piece of cellulose acetate tape (faxfilm) is pressed on the surface. Good contact is assured if the back of the tape is wetted with dioxane and rubbed until tacky. After allowing the solvent to evaporate, the tape is pulled from the specimen.

B. The acetate tape is scotch taped by the edges to a glass microscope slide with the impression side up. When a number of replicas are being made, which is usually the case, the slide should have an identification label.

C. The slides bearing the acetate impressions are placed in a fixture designed to hold them at 5 in. from the carbon source. The fixture consists of a piece of metal curved to a 5 in. radius and fastened to the base of the carbon evaporator. This unit has two 1/8-in.-diameter carbon rods one of which has a tip turned down to 0.040 in. about 1½ to 2 mm long. These carbon rods are positioned so that the 0.040-in. tip is held against the flat end of the other carbon by the spring pressure of the holder.

The assembled apparatus with the slides in place are connected to the electrical terminals, the bell jar placed, and the vacuum pumped (0.5 μm). Current is passed through the carbons until the tip glows, then the full power is applied. This instantly "burns off" the tip. The evaporation is complete, and the vacuum may now be released.

D. The carbon and plastic containing the particles now make up the positive replica as they conform to the detail obtained on the faxfilm as a negative replica. The next step is the removal of the cellulose acetate (faxfilm). Sections of the composite replica about 1/8 in. square are cut and placed on 500 mesh specimen screens with the plastic toward the screen. Usually several sections may be obtained, each on its specimen screen. These are placed on a table made of household window screen which is positioned in a glass dish to hold the specimen screens about ½ in. above the bottom. The dish is then filled with just enough acetone to wet the specimen screens by capillary attraction, covered, and allowed to set for about 30 min. By this time, most of the cellulose acetate will have been dissolved. The condition of the replicas should be examined at this time. The wide-field stereo microscope is used for this. If the replicas appear to be good (often some of them are not), the replicas are washed twice in fresh acetone by pipetting the used solvent out of the dish and replacing it with fresh, taking care to avoid filling above the screen level as the replicas may be washed off the support screens. Finally, lower the level of acetone in the dish. This allows the replicas to dry in an atmosphere of acetone vapor, avoiding too rapid drying.

E. The dried replicas and their individual support screens are transferred to electron microscope specimen holders and are ready for examination.

2.2.4 *Direct Carbon Extraction Replica*

In this method a negative of the surface is obtained by direct deposition of carbon. The steps involved are as follows:

A. The micropolished specimen is etched with a suitable reagent to attack the matrix leaving the particles loose and exposed.

B. This specimen is placed in a vacuum evaporator, and a moderately thick film of carbon is deposited at normal incidence.

C. The carbon film containing particles is stripped off the specimen by chemically dipping or electropolishing in a suitable electrolyte. (It sometimes helps to scribe small squares on the specimen surface to facilitate the attack on the matrix material.)

D. The small squares float off in the electrolyte from which they are removed on screens and thoroughly washed.

2.2.5 *Extraction Replicas Removed by Two Stage Etching*

The steps in this technique are shown schematically in Fig. 1.

A. The first step in the technique is identical to the plastic replica method. The specimen is polished, etched, and then covered with a thin film of a plastic such as parlodion or collodion.

B. Then the specimen is again etched through the plastic to free the particles exposed by the first etch. Most plastics are quite permeable to etching solutions, and the specimen etches almost as rapidly as without the plastic film.

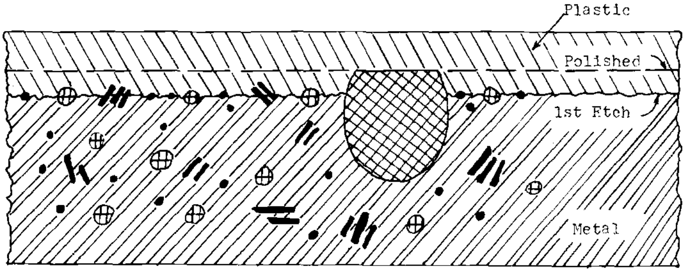
C. After etching, the surface is washed with flowing alcohol and dried with a gentle stream of warm air. The replica is easily stripped from the surface with scotch tape.

2.2.6 *Replication of Thin Surface Films*

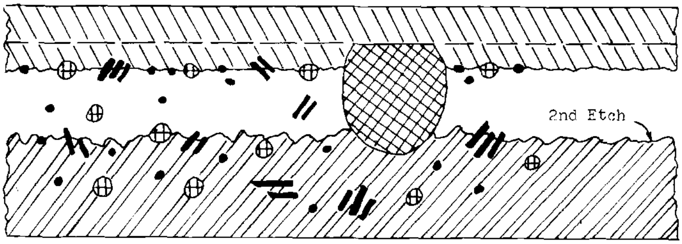
Surface films can be removed by numerous techniques, the methods generally used are:

A. *Strip and Flotation Method*

(*a*) Loosen the film from the surface by electrolyzing or other chemical



FIRST ETCH



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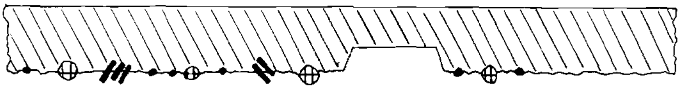

REPLICA

FIG. 1–*Extraction replica technique shown schematically (after Fisher*[7] *of Bibliography).*

means which attack the base material but leave the film unattacked. (It is often necessary to scribe the surface in small squares to facilitate film removal.)

(*b*) Float the film off in the chemical solution.

(*c*) Lift the film from the solution with 500 mesh screens.

(*d*) Dry the films thoroughly before using.

B. Films can also be removed by backing with a plastic or depositing a thin film of carbon on the surface. The backing material is scribed into squares, and the procedure in Section 2.2.6A. is applicable in this method.

2.2.7 *Aluminum Oxide Extraction Replica*

Aluminum and its alloys are especially well suited for oxide replication. Additionally, the oxide replica has the inherent qualities necessary for extraction techniques.

A. As-fabricated or polished or etched surfaces or both may be replicated as desired.

B. Replica formation is achieved in a 3 percent tartaric acid electrolyte adjusted to a pH of 5.5 with ammonium hydroxide (NH_4OH). The solution is employed at ambient temperature with the specimen as anode, a high purity aluminum cathode, and a forming potential of 20 to 25 V dc. The specimen is tapped frequently to dislodge evolved gas bubbles. Anodization time is usually 5 to 10 min.

C. Areas to be examined are selected and scribed as noted in Section 2.2.4C. Remaining areas are usually painted with a chemical resist. Selected replicas are next stripped from the specimen electrolytically at a potential of 12 to 15 V dc in 20 percent perchloric acid in denatured alcohol. The specimen is again made the anode, using a high purity aluminum as the cathode. Floated replicas are then treated as noted in Section 2.2.4D.

2.3 Tables of Extraction Replica Techniques

Table 1 lists extraction replica techniques for carbon steel, low alloy steel, high alloy steel, stainless steel, superalloys, and aluminum alloys; it also lists reference literature [*1-31*][2] on these alloys.

2.4 Bibliography

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[2] The italic numbers in brackets refer to the list of references appended to this chapter.

TABLE 1–*Extraction replica techniques.*

Alloy	Technique	Remarks	Ref
1. *Carbon steel:*			
Carbon steel	plastic carbon	comparison of techniques	[*8*]
Mild steels	plastic	investigation of large precipitates and inclusions	[*12*]
Steels	positive carbon	inclusions and precipitates	[*13*]
Iron-copper	positive carbon	copper precipitates in steel	[*14*]
Carbon steels	indirect plastic	large precipitates and inclusions	[*15*]
Aluminum killed low carbon steel	carbon	aluminum-nitrogen studies	[*16*]
Carbon steels	positive carbon	general morphology	[*18*]
Carbon steels	carbon	morphology of carbide	[*19*]
Pearlite		structure of pearlite	[*20*]
Pure iron	positive carbon	investigation of alumina inclusions	[*21*]
Low carbon	positive carbon	investigation of carbides	[*22*]
2. *Low alloy steel:*			
Molybdenum-boron	positive carbon	comparison of techniques	[*11*]
Chromium-molybdenum-vanadium	carbon	evaluation of carbides	[*19*]
3. *High alloy steel:*			
Tool steels, M2, M10, M21	plastic	study of grain boundary carbides	[*9*]
Maraging steel	positive carbon	study of aging kinetics	[*10,23*]
High speed steel, Fe-18W-4Cr-1V	direct carbon	general study of precipitates	[*28*]
4. *Stainless steel:*			
304		morphology of $Cr_{23}C_6$	[*4*]
410	direct carbon	morphology of nitrides	[*5*]
12Cr-4Ni	carbon	general precipitates	[*17*]
442	carbon	general precipitates	[*24*]
PH stainless	carbon	grain boundary carbide and matrix precipitates	[*25*]
17-7 PH	carbon	general precipitates	[*26*]

TABLE 1–(*Continued*)

Alloy	Technique	Remarks	Ref
5. *Superalloys:*			
Inconel X	plastic	identification of $Cr_{23}C_6$ and Ni_3Al (γ')	[*1*]
	direct carbon	identification of Ni_3Al (γ')	[*2,3,7*]
Waspaloy	direct carbon	identification of Ni_3Al (γ')	[*2*]
M 252	direct carbon	identification of Ni_3Al (γ')	[*2*]
Udimet 500	direct carbon	identification of Ni_3Al (γ')	[*2*]
NI55		minor phases	[*3*]
Cobalt base S816		minor phases	[*3*]
Iron base 16-25-6		minor phases	[*3*]
SM 200	positive carbon	identification of precipitate phases	[*6*]
Nimonic 80	plastic	identification of age hardening phases	[*27*]
5. *Aluminum alloys:*			
Aluminum	aluminum oxide	identification of minor phases, surface films, and oxides in SAP[b] or P/M[c] alloys	[*29,30*]
Aluminum	direct carbon[a]	major constitutent or certain precipitates or both	

[a] Use is generally preceded by etching the specimen in 10 percent bromine in absolute methanol at 150°F for 10 to 45 s for particle relief.

[b] SAP = sintered aluminum powder.

[c] P/M = powder metal.

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Task Group E04.11.03 [1]

Chapter 3—Thin Foil Preparation for Transmission Electron Microscopy

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3.1 Introduction

The desire and need to observe real structures and finer detail has resulted not only in higher performance electron microscopes but also resulted in a great deal of time and effort spent to design and develop better specimen preparation techniques. Since the first direct examination of thin metal foils in 1949 by Heindenreich[*1*],[2] many different methods of thin film preparation have evolved. This paper will not deal with transmission image interpretation but is intended as a review of procedures and basic techniques of thin foil preparation collected from literature and includes methods contributed by different laboratories represented on the American Society for Testing and Materials (ASTM) Subcommittee E04.11 on Electron Microscopy and Diffraction. Appendix 3.2 provides a complete bibliography of papers published in ASTM Special Technical Publications pertaining to thin foil preparation and applications of transmission electron microscopy of metals.

Direct examination of materials in the electron microscope in most instances requires a final specimen thickness of less than ½ μm. The starting material is usually much thicker; therefore, this report is divided into several steps of specimen preparation. The first section is starting with bulk material thicker than 500 μm (0.5 mm), second, intermediate or prethinning to approximately 50 μm (0.05 mm), third, final thinning techniques, and fourth, a section on special or unique thinning methods.

3.2 Bulk Thinning to 500 μm (0.5 mm)

3.2.1 *Cutoff Wheel*

The fastest and easiest way to get thin starting material is to cut thin sections of 1 mm or less using high speed metallographic abrasive cutoff wheels. These are usually manual-fed machines with liquid cooling. The less cutting pressure

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[1] Prepared by Albert Szirmae, U.S. Steel Corp.

[2] The italic numbers in brackets refer to the list of references appended to this chapter.

applied the thinner the slice that can be cut and the more uniform the thickness. The depth of deformation on a silicon-iron specimen cut with a cutoff wheel was measured by Szirmae and Fisher[*2*] to be about 200 μm. A more sophisticated version of the cutoff wheel is a machine shop precision wafering machine[*2*] that has a much higher revolutions per minute, thinner abrasive or diamond wheel, and an automatic feed. These features permit specimens to be cut to a thickness of 400 μm or 0.4 mm.

3.2.2 *Spark Machining*

Another method of cutting thin slices from bulk metal is to use a machine that creates an electric spark discharge[*3,4*] between the specimen and a thin metal blade or tool. Spark machine cutting has the advantage in that the tool does not come in contact with the material but automatically maintains a preset spark gap distance controlled by a servo motor. The spark causes micromelted pores at the sparked surface and results in less depth of deformation[*2*] than with any other cutting method. A modification or attachment can be added to spark machines to continuously unreel and draw a fine wire, about 75 μm in diameter over the specimen to cut thin slices 200 μm thick with no detectable deformation.

3.2.3 *Electrolytic Acid Saw and Acid Planning Wheel*

The electrolytic and chemical action of an acid coated Saran or Terylene thread moving in contact with the specimen is another method[*5,6*] of cutting strain-free slices of material to thicknesses of about 1 mm. An acid planing wheel[*6*], designed to work on this same principle, has also been used to prepare uniformly flat specimens to about 1.5 mm thickness. As early as 1961 Strutt[7] successfully used this acid planing method to prepare foils from metal tension specimens.

3.3 **Prethinning to 50 μm (0.05 mm)**

3.3.1 *Surface Grinding and Hand Grinding*

Once the specimen is in an ideally 0.5-mm-thick disk or rectangle about 2 cm^2, it can be further thinned by mechanical grinding. If the specimen is magnetic or can be held rigid and flat by a vacuum or clamps, a machine shop surface grinder is a good tool to make the specimen uniformly thin with parallel surfaces. In 1957, Samuels and Wallwork[*8*] performed a comprehensive investigation of the nature and depth of deformation of machine and hand grinding. They found that the depth of gross deformation was between 5 and 10 times the depth of the abrasion scratches. This indicates that as the specimen is ground thinner, lighter cuts or passes should be made with a surface grinder. If a surface grinder is not available, hand held grinding on a circular metallographic grinding wheel is recommended. The specimen can be held with double sided scotch masking tape on a flat metal block or blank bakelite mount of suitable size to permit easy griping and to ensure a flat finished surface. The specimen should be ground from both sides by carefully removing it, checking the thickness with a micrometer, and remounting it to grind the other surface. By systematically advancing from 220 grit to 600 grit papers, the specimen can be ground to 100 μm (0.1 mm) or less. To remove the thinned specimen from the tape, dissolve the adhesive in xylene or toluene until the specimen lifts off easily without bending.

3.3.2 *Cold Rolling*

If the cold-rolled microstructure is not of interest or if the specimen can be heat treated for a required structure, hot or cold rolling can be used for prethinning. Material can be rolled to 50 μm (0.05 mm) with a uniformly smooth surface if it does not work harden or if it is not brittle.

3.3.3 *Chemical Prethinning*

When mechanical methods of prethinning are limited due to the shape or size of the specimen, chemical thinning can sometimes be used. The edges of the specimen should be painted to prevent edge attack or preferential thinning from reducing the size of the specimen. Keown and Pickering[*9*] have used successfully chemical prethinning for different kinds of steels, such as stainless, low alloy, high alloy, and carbon steel. Davy et al[*10*] describe a very fast method of chemical prethinning low alloy and ferritic-chromium steels. A fairly complete list of chemical polishing solutions and conditions is given in table form for about 38 different elements and alloys by Hirsch et al (4 of Appendix 3.1).

3.3.4 *Electrolytic and Jet Prethinning*

In some instances this may be a faster method than chemical prethinning. The edges of the specimen should be painted with an insulating lacquer to prevent preferential attack at the edge. The fast polishing solutions are recommended for prethinning and should be kept cool by mechanical stirring or agitation and cooling coils to prevent heat buildup at the specimen surface which results in etching. The electrolyte and specimen size and shape of specific materials will vary the voltage, current, and time required, but the material should be prethinned to 50 to 75 μm (0.05 to 0.075 mm) before final thinning. Kelly and Nutting[*11*] have used successfully electrojet machining to prethin martensitic steels from 1 mm to about 0.1 mm.

3.4 **Final Thinning to Less Than 0.5 μm**

3.4.1 *Bollmann Method*

One of the earliest accepted methods of electropolishing was the Bollmann method[*12*]. Many modifications of this technique have evolved, but the principle remains the same. The anode is a disk or rectangle about 2 cm^2 and 0.05 mm thick with insulating paint, lacquer, or varnish painted around the edge on both sides. The specimen is held rigid and vertical with tweezers or a metal clip and is immersed in an electrolyte. Two cathodes which are pointed metal rods, 3 to 5 mm in diameter, painted except for the points, are placed about 2 mm distance from the center of the disk on each side. In this position the polishing occurs at the center of the specimen, and, when a small hole forms, the cathodes are moved further apart to about 1 cm distance from the specimen so that the polishing is more concentrated at the outer edge until another hole forms. Polishing is continued only until the two holes enlarge and are about to join. After the specimen is rinsed and dried, the bridge or area between the two holes can be cut out and examined in the electron microscope because large thin regions are usually present in this area along the polished edges. Variations of this technique include different configurations of the cathodes such as blunted rods, metal rings or washers, a wire spiral in the shape of a cone, or even a plain stainless beaker or dish. Fisher and Szirmae[*13*] describe a technique of clamping two metal rings or washers around the outside edge of the specimen for rigid support and more uniform electropolishing of stainless steel foils. A similar conductive mask technique has been developed by Despres[*14*] and is being successfully used for ferrous and nonferrous alloys. In this method an 0.1-in.-square specimen is cut from 0.00075-in.-thick prethinned material and is sandwiched and spot welded between two small stainless steel washers which are held by special metal forceps acting as the anode lead. The main advantages are that the electropolishing time is short, and minimum handling is required because the whole sandwich assembly can be placed into the microscope after rinsing and drying.

No one solution or voltage is adequate for all materials, but the basic potential versus current density curve as described by Thomas (2 of Appendix 3.1) provides a good general reference for determining the right polishing conditions for each solution. A high polish with minimal etching usually occurs on the flat or plateau portion of the curve as explained by Tegart (1 of Appendix 3.1) for copper and Glenn and Raley[*15*] for iron.

3.4.2 *Window Method*

This method, first developed by Nicholson[*16*] uses a flat vertically suspended specimen (larger than the Bollmann specimen) as the anode and also uses two flat vertical cathodes about 2 to 3 cm away from the specimen which are held parallel to both sides of the specimen. The edges of the specimen also should be insulated with lacquer. As polishing progresses, perforation usually occurs at some point near the top edge and advances downward. Brammar (5 of Appendix 3.1) and Thomas (2 of Appendix 3.1) both have a good explanation and a few clear sketches that show the different stages of polishing by this window technique. In some instances a better polish results if the current is switched off and on a few times prior to removing the specimen from the electrolyte. Copper specimens which oxidize very rapidly should be removed (without switching the current off) from a nitric acid-methanol electrolyte which is covered with a layer of liquid nitrogen and immediately rinsed in cold (–20°C) methyl alcohol. An improved window method described by Glenn and Raley[*15*] using a low-voltage thinning apparatus with a hole in the flat cathodes and results in consistently good foils with little rise in specimen temperature during polishing.

3.4.3 *Disa Electropol Polishing*

This technique, first developed by Mirand and Saulnier[*17*] in 1958 uses a regular commercial electrolytic metallographic polishing unit which polishes thin foils and allows small fragments to drop into the electrolytic reservoir. The small fragments are collected with tweezers and are usually good thin specimens if they are not deformed or etched by their stay in the electrolyte. Modifications to this basic unit and technique, as made by Hugo and Phillips[*18,19*], have increased the versatility and speed of obtaining good foils.

3.4.4 *Chemical Polishing*

Final chemical polishing is somewhat limited to pure metals and single phase materials because of preferential attack of some alloys and phases. Certain crystallographic planes and certain substructures are also sometimes etched, which prevents clear interpretation of the image in the electron microscope.

3.4.5 *Electrolytic and Automatic Jet Polishing*

Jet polishing can be used effectively to prepare specimens from specific areas of interest, because the electrolyte can be directed to impinge on certain areas. In addition, by using two jets, one from either side, as Hugo and Phillips[*20*] reported, an added advantage is a reduction in polishing time. Final jet polishing can also be done on large or small specimens and can be immersed in the solution or suspended out of the solution. One of the main advantages of automatic jet polishing, as reported by Schoone and Fischione[*21*], is that a specimen from the prethinned specimen can be punched out as a small disk the size of normal electron microscope grids. This disk can then be supported in specially designed holders[*21,22*] and be jet polished in automatic electropolishers.

The specimen holder, usually made of an insulating material such as Teflon or polytetrafluoroethylene (PTFE) which is unaffected by electrolytes, not only supports the specimen but provides support for the electrical contact platinum wire. The holder also protects the specimen edge from electrochemical attack, thereby enhancing the thinning process near the center. The polishing unit also contains an automatic shutoff circuit using light wires and a photocell to stop the polishing at the first sign of a hole in specimen. This type of metal disk specimen can be mounted directly in the electron microscope with less chance of deformation than mounting cut specimens. Supporting grids are not necessary unless the thinned areas are very fragile. Presently, automatic jet polishers similar to the one described by Schoone and Fischione[*21*] are commercially available for polishing punched out disk specimens.

3.5 Unique Thinning Techniques

3.5.1 *Small Diameter Wires*

Thin foils from the cross section and longitudinal section of steel and copper wires as small as 0.13 mm (0.005 in.) in diameter have been prepared by Glenn and Duff[*23*]. Their technique consists essentially of embedding the wires in plated nickel, grinding the composite to expose the wires, and electropolishing the nickel and wire from both sides using two polishing jets[*24*]. Earlier, Meieran and Thomas[*25*] made transmission foils from 0.75-mm (0.030-in.) diameter tungsten and molybdenum wire using a gravity flow jet prethinning technique and polishing apparatus similar to the one used by Wilsdorf et al[*26*]. Stickler and Engle[*27*] describe a technique for preparing foils from fine wires less than 1.0 mm (0.04 in.) in diameter by grinding, microjet machining, and then using bath electrolytic polishing for the final step.

3.5.2 *Microtomy*

Microtomy of metals has not developed into a major specimen preparation technique even though it is fast and easy. However, Tice and Lasko[*28*] were successful in using a microtome to slice specimens from copper wire with synthetically encased lead filaments. Although deformation of the specimen is the main disadvantage, the size, shape, and distribution of the filaments can be observed much better than by using other techniques. In 1960, Phillips[*29*] showed clear evidence of the feasability of using an ultramicrotome to cut slices 100 to 600 Å thick from a variety of nonferrous metals and alloys. Ahlers and Vassamillet[*30*] reported in 1968 on the deformation structure of microtomed specimens of face centered cubic metals and alloys as compared with the deformation of electrothinned specimens.

3.5.3 *Ion Micro Milling*

The most recently developed thinning method is ion micromachining. This technique consists of having two intense, relatively low energy plasma beams to simultaneously sputter both sides of a rotating specimen inside a vacuum chamber with viewing ports for observing the milling process. Although it has been sucessfully used for thinning metals and alloys, the main advantage and use thus far has been to thin nonmetals and minerals as reported by Barber[*31*] in

1970, such as brick, cement, coal, and precious stones. The principal disadvantages are the complexities of the instrument and the long times required for proper thinning. Castaing[*32*] as early as 1955 originally used this principle to thin aluminum by ion bombardment directly in the electron microscope. Due to the slow rate of metal removal, which is about 1 μm/h, ion milling has not been developed for everyday use until recently. This method of making thin films for transmission electron microscopy is being presently used for ceramic materials, semiconductors, meteorites, and even lunar rocks as reported by Radcliffe et al[*33*].

3.6 General Precautions

3.6.1 *Mixing Electrolytes*

The basic chemistry rules for mixing acids should be strictly adhered to when mixing any electrolyte. All polishing procedures should be carried out under an adequate hood with good ventilation. Safety glasses should always be worn, and plastic or rubber gloves are necessary with some electrolytes. Tegart (1 of Appendix 3.1) devotes a chapter to the use of very reactive electropolishing solutions and lists many references for articles on safety precautions. A cardinal rule is to mix electrolytes slowly and to keep the solution cool.

3.6.2 *Polishing Film and Staining*

Some polishing solutions leave an obvious dark layer or film on the specimen that rinses off very easily in the electrolyte or in alcohol. In some cases, the film or stain is not evident until the specimen is examined at high magnification in the electron microscope. This usually transparent amorphous film such as that which forms on polished silicon iron specimens must be dissolved away in a mild solution of 50 cm^3 of methyl alcohol with 3 or 5 drops of hydrochloric acid or hydrofluoric acid. The specimen should be dipped in and out of the solution for a few seconds to dissolve only the amorphous film and not to etch the surface or thin edge. If the specimen is stained or etched to the point where structural features are obscured, it is possible to touch up or repolish the specimen to get a better surface. Polished specimens should be viewed in the microscope as soon as possible after the final polish or they should be stored in evacuated dessicators to prevent any oxide or contamination from forming on the surface.

3.6.3 *Electrolyte and Specimen Temperature*

The most important factor in polishing different metals and alloys is to choose the correct electrolyte. Appendix 3.1 lists 7 references that cover nearly every type of electropolishing solution and the best conditions to obtain a satisfactory mirror-like finish.

The rise in temperature of the solution during polishing decreases the viscous layer at the anode, lowers the resistance, and results in an increase in the current density and causes etching. To prevent these changes the electrolyte should be cooled by using an ice bath around the solution or cooling coils immersed in the solution. Care should be taken not to cool the solution to the critical point where precipitation and crystallization of some acids occur. Agitation or stirring the solution is helpful to maintain a more uniform temperature of the bath and prevent excessive local heating. Cox and Mountford [*34*] in a rare article on electropolishing temperatures, report a greater increase in specimen temperature with small 3-mm PTFE type specimens than with the larger Bollmann type specimen. This could be due partly to the much higher current densities with the small disk specimens.

3.6.4 *Cutting and Mounting*

When the Bollmann or Window method is used for the final polish, the specimen should be cut on a hard surface such as Lucite or Plexiglass using a sharp scalpel or razor blade so little or no deformation occurs at the thin polished edge. A sharp blade and care cannot be over emphasized because unintentionally induced deformation may change the appearance and structure of an annealed or heat treated material. For some materials it is better to cut the small specimens while the polished specimen is immersed in alcohol or in the rinsing solution. The specimen is then dried by blotting both sides with smooth absorbing filter paper and mounted between microscope grids. Folded 75 mesh sandwich-type grids are more convenient to mount the cut specimens than two loose grids because the folded grids are hinged and the grid bars coincide above and below the specimen. If the grid bars interfere with the viewing area, the center grids may be easily cut out before folding the grids and mounting the specimen.

For punched-out polished disk specimens, support grids are not usually necessary unless the polished edge around the hole is very fragile. If the specimen is very thin and magnetic, it may be bent by the force of the magnetic field of the objective lens, or, if it is a nonmagnetic specimen, it may just buckle from local heating of the beam. In this case the specimen should be allowed to stabilize to prevent image drift on the photographic plate.

3.7 Summary

Electropolishing is the most widely used method of thin foil preparation today. However, although many papers have been written explaining specific thinning techniques in great detail, when the method is first tried, it is not always successful. This is due mostly to the differences in power supplies and agitating conditions because polishing units and cathode and anode configurations can alter the required current densities. Needless to say, good thin foils have been prepared on simple homemade laboratory polishers, as well as with elaborate commercial units. Consistently good results seem to occur only after a little experience and trial and ertor in setting up one's own techniques and conditions for a specific material.

3.8 Acknowledgments

Subcommittee E04.11 on Electron Microscopy and Diffraction of ASTM E-4 wishes to thank all those members who contributed their time and polishing techniques to make this report possible.

APPENDIX 3.1

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Chapter 4—Selected Area Electron Diffraction Analysis of Extraction Replica and Thin Foil Specimens in the Transmission Electron Microscope

4.1 Introduction

This procedure is intended as a guide for satisfactory selected area electron diffraction (SAED) analysis in the transmission electron microscope (TEM), of extraction replica and thin foil specimens. It is intended to help those who have a minimal understanding of crystallography but desire to use electron diffraction analysis for identification of precipitates or determination of their orientation (or orientation of other substructural features) relative to the matrix or both. A stepwise outline form is presented of the procedures to be followed without much theoretical background; however, a list of references[*1-6*][2] is provided to supplement this procedure with as much theory as is desired. Two examples of the application of the procedure are also given.

Part I includes some information on preparation of extraction replicas, and, in more detail, procedures and precautions for preparing and indexing SAED ring and spot patterns for the replica extracted particles and for identifying the particles. The indexing and interpretation described are particularly applicable to cubic materials. Part II describes procedures which were worked out specifically for SAED analysis of thin foil specimens of a hexagonal metal, and this accounts for some of the differences between Parts I and II. Other differences simply reflect alternate but equally valid ways of handling the solution and interpretation of SAED patterns and the crystal structures and substructures they represent.

Appendixes are provided which describe in some detail the solutions of two actual problems in selected area electron diffraction analysis of cubic precipitates; one for an extraction replica and one for a thin foil specimen. In addition,

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[1] Prepared by C. W. Andrews, NASA-Lewis Research Center; Halle Abrams, Bethlehem Steel Corp.; and Albert Szirmae, U.S. Steel Corp.

[2] The italic numbers in brackets refer to the list of references appended to this chapter.

the appendixes include: (1) an alternate method for calculating the electron microscope camera constant; (2) equations relating interplanar spacing *d*, lattice parameter *a*, and radial displacement of diffracted beams *r*, to the Miller indices *h, k, l*; (3) a table of electron beam wavelength, with and without relativistic correction, as a function of beam accelerating voltage; and (4) allowed body centered cubic (bcc) and face centered cubic (fcc) "reflections" and their *h, k, l* relationships.

PART I—PARTICLE OR SECOND PHASE IDENTIFICATION USING EXTRACTION REPLICA AND SELECTED AREA ELECTRON DIFFRACTION

4.2 Introduction

One of the early methods of particle or precipitate identification utilized the analysis of X-ray or electron diffraction patterns of material physically separated from the bulk matrix by the extraction replica technique. This method is still widely used today and can be accomplished with a great deal of accuracy using X-ray diffraction analysis if the second phase is of sufficient quantity. However, if the size and number of precipitates are small, then electron diffraction is more appropriate because less bulk material is necessary, and the size, shape, and number or amount can be determined in the electron microscope in addition to identification by diffraction patterns from the particles.

4.3 Technique for Preparing Extraction Replicas

A. Due to the many variations and versions of techniques for preparing extraction replicas which have become available since the method was first devised by Fisher[7] in 1953, the details of specific techniques will be left to the reader to extract from the list of provided references[*1-7*]. The most recent compilation of the extraction replica techniques may be found in Chapter 2. Only a few general remarks will be made here for making good extraction replicas, since the primary purpose is to present a technique for obtaining and analyzing corresponding electron diffraction patterns and images from the replicas.

B. The chemical or electrolytic etchant must have the capability to dissolve the matrix and not affect the desired precipitate phase.

C. The number of extracted particles is controlled by the length of time allowed for the initial and final etch and, of course, by the size of the particles. The final etch takes many times longer than the initial etch, but the time can be decreased if electrolytic techniques are employed. If identification is of prime concern, then the replica should contain as many particles as possible to provide a sharp and continuous ring pattern. However, one should generally avoid excessive final etching times, since it is possible for continuing slow attack of the extracted particles by the solution, or accumulation of insoluble "sludges," to alter the effective composition and hence the diffraction pattern. If orientation relationships or shape and size are wanted, then it is desirable to have fewer particles because single crystal spot patterns must be obtained from individual particles. In some instances, single particles are too small to yield a sufficiently intense spot pattern, and, in other cases, the particle may be too thick for the beam to penetrate. The latter problem has been alleviated somewhat with the advent of high voltage electron microscopes because smaller diffraction apertures can be used and more penetration is evident.

D. The substrate or supporting film can be oxide film, carbon, or any of the plastic replicating materials with carbon being the most widely used because of its insoluble chemical properties and good stability in the electron beam.

4.4 Indexing Selected Area Electron Diffraction Patterns

4.4.1 *Calibration of the Microscope Constant*

A. For solving transmission selected area diffraction patterns of extraction replicas, the most important initial step is to determine the electron microscope camera constant (K) from a diffraction pattern of a known material. Normally, this is obtained from a standard or a thin evaporated metal film of gold, palladium, chromium, etc., that gives a sharp ring pattern. The standard may also be purchased on a grid ready to use from any microscope accessory supplier.

B. Measure the radii (r) of the rings and calculate the camera constant (K) by multiplying the radii by the corresponding d spacings:

$$K = r\,d \tag{1}$$

where r is the measured distance in millimeters from the central spot to a ring and d is the interplanar spacing in angstroms taken from the ASTM X-ray index file for the corresponding material and ring. There are commercially available densitometers and diffractometers to measure accurately and elaborately the diffraction patterns, but, if these instruments are not accessible, then the pattern should be measured directly from the emulsion side of the photographic plate back illuminated with a light box. The measurements should be made using about a X5 magnifying glass, a pair of pointed dividers from a drawing set, and a metal millimeter ruler. The constant (K) can be calculated from more than one plate and then set up in table form specifically listing the exact operating conditions. The camera constant (K) obtained in this way is useful only if identical operating conditions prevail during the exposure of diffraction patterns from the unknown material. Andrews[2] gives a very thorough section on accuracy related to physical factors, but it is sufficient to say here that it is most important to use the same accelerating voltage and lens currents for the standard and unknown pattern. However, some small variations or errors will be evident when the constant is calculated from one day or week to the next due to errors in measurement, changes in specimen position, or voltage or lens-current fluctuations.

C. Changes in specimen position along the microscope axis, often encountered from one thin foil specimen to another, require changes in objective lens (OL) focus. The resulting variations in OL current produce corresponding variations in *K*. This source of variation in *K* can be corrected for by obtaining a calibration of *K* versus OL current as follows: A grid with evaporated gold on carbon is inserted into the microscope tilting stage. Nearly all tilting stages are sufficiently imperfect so that the position of the specimen along the microscope axis varies significantly as the stage is tilted to its extremes. Therefore, a field of the specimen near the periphery of the grid is selected, and, as the stage is tilted, specimen image refocussed, and *K* remeasured, a broad range of OL currents and corresponding values of *K* are obtained and plotted. The operator then needs only to record the objective lens current when photographing an unknown diffraction pattern and refer to the *K* versus OL current graph. Of course, for critical examinations, or if there is evidence of drift in *K* from other factors (see 4.4.1B), a new determination of *K* should be made. *K* for a given OL current has been observed to remain constant for a week to a month within plus or minus 1 in the third significant figure. Faster drift suggests deterioration of reference-voltage batteries, (if these are used), and they should be changed as a first countermeasure.

D. In the following method of calculating the camera constant simultaneously with the identification of the unknown compound, some errors due to changes in microscope operating conditions can be eliminated by evaporating a thin layer or film of the known standard directly on the extraction replica. The limitation here is, if the unknown gives a ring pattern then the standard should give a good sharp spot pattern as does thallium chloride, or, if the unknown is a spot pattern, then the standard should be a thin metal film standard to give a ring pattern. If the standard material is evaporated at an angle on to the unknown through a specimen grid, the shadowed areas will contain both standard and unknown material, while the unshadowed areas will consist of only the unknown material. By comparing diffraction patterns of the two areas, it can be determined if any ring of the unknown pattern is superimposed on a standard ring. Thus, if the standard rings can be distinguished from the unknown pattern, then this simultaneous diffraction method is more accurate than using separate grids with standard material.

E. Another method of calculating the same camera constant (*K*) which does not require measuring diffraction patterns is given in Appendix 4.1. However, the simultaneous diffraction methods just mentioned are recommended because they provide confidence in the measurements and reveal any changes that may have occurred with the microscope.

4.4.2 *Identification of Unknown Ring Diffraction Patterns*

After the camera constant (K) has been determined, it is possible to analyze or identify an unknown pattern from the precipitates or particles in the extraction replica. It is important to note here again that the operating conditions of the microscope must be identical to the conditions when the standard pattern was taken. The procedure for measuring the radial distance of the unknown rings is the same as for measuring the rings of the standard. It is recommended that these distances be listed in table form and the corresponding d values calculated and listed in the same table using the equation

$$d = K/r \tag{2}$$

where K is the previously determined camera constant and r is the measured radial distance in millimeters. Knowing the d values or interplanar spacings, the next step is to identify the unknown material by correlating the calculated d values to the closest matching set of actual d values found in the ASTM Diffraction File Index. The arrangement or symmetry of the rings can sometimes indicate whether the crystal structure is fcc or bcc. If the rings are paired with a single ring in between as a double ring, single ring, double ring, single ring, etc., the structure is probably fcc. It is not uncommon to find 2, 3, or even 4 sets of values that closely match the calculated d spacings. The true identity of the unknown element or compound should be established from available information about the original material, its composition, heat treatment, etc. If identification is still not possible after more patterns have been measured, then it may be assumed that the ring pattern could be from more than one type of precipitate or particle. This can sometimes be discerned by using a very small selected area diffraction aperture (10 to 5 μm across) to try to limit the diffraction pattern to a single particle.[3] In this case, the pattern probably will be a single crystal spot pattern which can be measured in the same way as the ring pattern, but now it is necessary to index the spots to know which planes the spots and d values are corresponding to.

4.4.3 *Indexing Simple Single Particle Spot Patterns*

A. This portion of the procedure will be limited to the cubic crystal system for simplicity and is intended as an introduction to indexing electron diffraction

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[3] The term "selected area aperture" as used here generally refers to either of the two common types: (*a*) A series of circular apertures arranged in order of decreasing size on a common click-stop insertion shaft. Each aperture may be adjusted for X and Y position, and this arrangement is fast and convenient to use. (*b*) A set of three or four blades which form a triangular or rectangular aperture opening of continuously variable position, size (and for the rectangular arrangement, length-to-width ratio) is used. The rectangular arrangement is somewhat more versatile but is definitely more time consuming to position and adjust.

patterns of essentially single crystal phases. Some aspects of indexing diffraction patterns of noncubic crystals are considered in Part II.

B. Most of the electron microscopes capable of selected area diffraction analysis using 10 to 5 μm diffraction aperture sizes are also equipped with some sort of goniometer specimen tilting stage. This provides the ability to tilt the specimen to some angle that results in a low index spot pattern from the intended particle. If a tilting stage is not used, then different particles should be tried to find one that gives closest appearing spots because this indicates a lower index basic pattern which is easier and less complicated to index.

C. The first step is to measure the radial distance, r, in millimeters of 3 spots that form a parallelogram (not necessarily a rectangle) including the central spot, as shown in Fig. 1.

D. Arithmethically square the measured radius values.

E. Divide through the lowest squared value so 1 is the ratio for one of the spots (nearest to the central or undiffracted beam spot).

F. Multiply each ratio by the smallest integer that will raise the ratios to approximately whole numbers.

G. Each of these whole numbers will be equal to the value of $(h^2 + k^2 + l^2)$ for the corresponding spot, because in the cubic system the square of the radius is proportional to the sum of $(h^2 + k^2 + l^2)$ as

$$r^2 \alpha (h^2 + k^2 + l^2) \tag{3}$$

where (hkl) are the Miller indices of the planes corresponding to the spot being considered at radius r on the diffraction pattern. Therefore, it is possible to tentatively index the three measured spots with the corresponding hkl, as shown in Fig. 2. An aid to distinquish between fcc and bcc structures is: For any given spot, h, k, and l must be all odd or all even numbers for fcc, and the sum of $(h^2 + k^2 + l^2)$ can only be even for bcc. Table 1 lists the allowed reflections in the fcc and bcc crystal systems for the low index Miller indices. The spots should be measured directly on the plate, but an enlarged photograph or tracing should be used for actual numbering and indexing, and for measuring or checking angles.

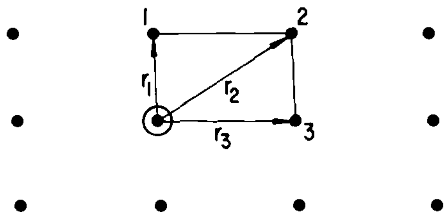


FIG. 1—*Selection and measurement of radial distances* r_x *to three diffracted spots forming a parallelogram.*

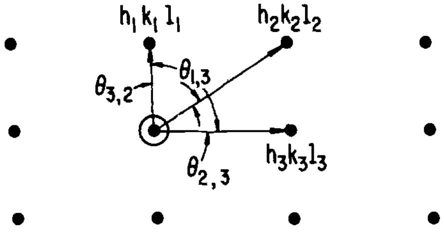


FIG. 2—*Designation of indices and angles for three diffracted spots of Fig. 1.*

H. The *d* values can now be calculated using Eq 2.

I. The next step is to measure the angles (θ) between the indexed spots on the enlargement or tracing using a protractor. The real or actual angles can be obtained from tables of Angles Between Planes of the Cubic System as in Cullity [5] or by calculating the angle (θ) by using the following equation:

$$\cos\theta_{1,2} = \frac{h_1h_2 + k_1k_2 + l_1l_2}{(h_1^2 + k_1^2 + l_1^2)(h_2^2 + k_2^2 + l_2^2)} \tag{4}$$

If the measured angles correspond closely (that is, about ±2 deg) to the calculated or actual angles, it can be assumed that the labeling of the three spots

TABLE 1—*Permissible reflections of low index Miller indices in the cubic crystal system.*

Simple Cubic, *hkl*	$h^2 + k^2 + l^2$	$\sqrt{h^2 + k^2 + l^2}$	fcc	bcc
100	1	1.000		
110	2	1.414		110
111	3	1.732	111	
200	4	2.000	200	200
211	6	2.449		211
220	8	2.828	220	220
300,221	9	3.000		
310	10	3.162		310
311	11	3.316	311	
222	12	3.464	222	222
320	13	3.605		
321	14	3.741		321
400	16	4.000	400	400
331	19	4.358	331	
420	20	4.472	420	420

in 4.4.3.6 is correct as to the family or type of plane. It is recommended that 2 or more other spots be measured and calculated as in 4.4.3C through 4.4.3I.

J. A check at this point is necessary to see if the indexing is consistent, that is, the type of plane may be correct but the sign of the Miller indices may not be. The signs can be checked by vector addition, that is, $h_1k_1l_1 + h_3k_3l_3 = h_2k_2l_2$ (see Fig. 2). If this calculated $h_2k_2l_2$ does not agree with the indexed $h_2k_2l_2$, this means that $h_1k_1l_1$ or $h_3k_3l_3$ does not have the correct sign. The easiest way to find the correct sign is to compare the pattern to a known standard indexed spot pattern in Appendix 5 of Hirsch[*3*] or in Kay[*1*]. Another method is to check a standard (001) stereographic projection of a cubic crystal by assigning some $h_1k_1l_1$ to spot 1 of the type previously determined and knowing the angle between spots 1 and 3, determine the correct sign of $h_3k_3l_3$ for spot 3, and then calculate $h_2k_2l_2$ by vector addition as further illustrated in Appendix 4.3.

K. If the indexing thus far is consistent, then the spots diametrically opposite and equidistant from the center spot can also be indexed because they are associated with the same set of crystal planes and related by a change of sign, as shown in Fig. 3. Spots in a straight line with the center spot are related by $h_3k_3l_3$, $2(h_3k_3l_3)$, $3(h_3k_3l_3)$, etc., as the distance increases as is shown in Fig. 3. In this manner, once 3 or 4 basic spots are indexed correctly, the remainder of the pattern can be easily indexed. It should be kept in mind that the relative intensities for X-ray patterns, as listed on the ASTM Index Cards, bear no relationship to the relative intensities of the rings or spots of the selected area electron diffraction pattern. A single crystal spot pattern is unlikely to contain all of the reflections listed on the cards, but a good ring pattern will.

L. For cubic crystals the lattice parameter (a) can be calculated for each spot using the equation normally written in the form $1/d^2$, and then averaged:

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} \qquad (5)$$

or

$$a = \sqrt{d^2(h^2 + k^2 + l^2)} \qquad (6)$$

where d is the calculated interplanar spacing and hkl are the assumed Miller indices. If the foregoing step by step procedure from 4.4.3C through 4.4.3L is followed, the pattern should be correctly indexed, the d values tabulated, and the lattice parameter calculated. With this information and a thorough search of the ASTM Index, the unknown particle, precipitate, or phase should be identifiable.

M. If the spots cannot be consistently indexed, the crystal structure may not be cubic but one of the other crystal systems. Appendix 4.2 lists the equations

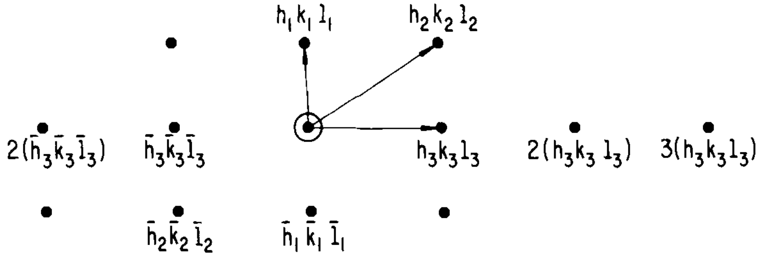


FIG. 3—*Indexing of diametrically opposite spot and spots of increasing diffraction order* (n) *for the diffraction pattern of Fig. 1.*

that can be substituted for Eqs 3 and 5 to see if the crystal structure is hexagonal or tetragonal. If the resultant ratios of 4.4.3F are not arithmetically simple and spots are still not consistent when assigning Miller indices, then the crystal structure is not hexagonal or tetragonal but is one of the remaining crystal systems and can be analyzed by referring to Andrews[*2*] or Hirsch[*3*]. It should be mentioned at this point that there are special cases when the pattern appears to contain extra or spurious spots. These may be complicating diffraction effects caused by stacking faults, thin twins, ordered regions, or superlattice structures, as is explained in more detail by Hirsch[*3*] and Thomas[*4*]. If the crystal structure is noncubic, or if more than one phase is present, double diffraction effects also often complicate the diffraction analysis. See Appendix 4.4.

N. The lattice orientation of a particle or phase can also be calculated, that is, the pole of that lattice plane (of the particle) which is lying perpendicular to the electron beam when the diffraction pattern is taken, is the zone axis of the pattern. The orientation or zone axis is usually specified as [*uvw*] and is calculated from:

$$u = k_1 l_2 - l_1 k_2$$

$$v = l_1 h_2 - h_1 l_2$$

$$w = h_1 k_2 - k_1 h_2$$

As a check for spots around the center of the pattern, all the indices should satisfy the condition

$$hu + kv + lw = 0$$

For a cubic particle, the orientation of the particle and the zone axis of the pattern is then [*uvw*].

O. If the precipitate lattices have specific orientations relative to the matrix lattice, these can be obtained by knowing the rotational relationship[*1,4*] between the diffraction pattern and micrograph. This rotational relationship can be calibrated for individual microscopes by indexing spot patterns of molybdenum trioxide (MoO_3) because the axis or crystallographic direction of the long straight edge of the MoO_3 crystal is <100>. By taking the micrograph and diffraction pattern separately or superimposed with a double exposure, the angle of rotation from a micrograph at any magnification to the pattern can be easily measured. However, as in the case for calibrating the microscope camera constant (K) the rotational relationship between the diffraction pattern and the micrograph is dependent upon the operating conditions, that is, accelerating voltage and lens settings. In this case, a calibration of rotation versus magnification (or equivalently, versus intermediate lens current) can be made for each accelerating voltage. If the position of the specimen along the microscope axis (or equivalently, variations in OL current) are found to be significant, then rotation calibration curves can be determined also for each of several values of OL current (see section 4.4.1C).

Another method of rotation calibration has been suggested[*9*] which does not require preparation of a MoO_3 crystal but uses instead the image and "diffraction pattern" of a rectangular selected area aperture. This appears quite feasible for an electron microscope having the 4-blade type selected area aperture; however, details are not given here but are available in the reference.

4.5 Summary

Part I of this procedure is intended for anyone trying to identify precipitates or a second phase using the extraction replica technique and electron diffraction analysis. It is not meant to make the identification of unknown material an easy chore, because the ease only develops with the number of times or occasions indexing is actually carried out. It is possible to recognize types of patterns and systems directly on the microscope screen, but exact identification, even with much experience, is sometimes difficult due to errors in measurement, change in conditions, specimen height, or sometimes having to work with a bad pattern with too few and not intense enough spots. Also, diffraction patterns for noncubic crystals can appear deceptively simple or symmetrical. For example, for a hexagonal crystal, what appears on the microscope screen to be a perfect diffraction pattern for the basal plane oriented normal to the electron beam (hexagonal symmetry), may in fact be the pattern for a pyramidal plane normal to the beam. The pattern actually will then be slightly elongated in one dimension from perfect hexagonal symmetry, sometimes so slightly that it can be detected only by careful measurement.

5.2 If the steps 4.4.3C through 4.4.3M fail to identify the extracted phase, the possibility of a noncubic crystal structure should be considered, and some assistance may be gained from reading Part II of the procedure. It is also suggested that other analytical methods such as X-ray fluorescence analysis be applied to the problem. Appendix 4.3 provides an actual step-by-step example of solution of a problem in identifying precipitates in an iron-columbium alloy [*9*].

PART II–ANALYSIS OF CRYSTALLOGRAPHIC FEATURES AND DEFECTS IN THIN FOIL SPECIMENS

4.6 **Introduction**

The electron diffraction analysis technique outlined here is useful for determining the orientation of a single crystal region (or of features in it) in a thin foil specimen, relative to the electron microscope beam axis. The features may be precipitates, dislocation substructures, or related "defects" in a foil specimen thinned from bulk material, which is examined directly in the transmission electron microscope (TEM); that is, the specimen is not replicated. While some details of the technique may be useful in phase identification, an electron diffraction analysis procedure for this purpose has been described in Part I of this procedure.

The technique described here was worked out specifically for a hexagonal close packed (hcp) metal. This may account for some of the differences in detail relative to Part I, which is based on analysis of extraction replicas of cubic phases. In addition to these differences, Part II of the procedure provides another approach to diffraction analysis which may help develop the insights required for successful solving of a wide range of SAED problems.

Crystallographic features and their characteristics of interest here include slip planes, slip-trace directions, Burgers vectors, twin orientation relationships, and precipitate-matrix orientation relationships, as well as grain and subgrain relative orientations. At least some familiarity with such standard references as Thomas [*4*], Hirsch et al [*3*], and Andrews et al [*2*] is assumed. It is helpful to have been at least introduced to the concepts of two-beam condition, reflecting (Ewald) sphere, reciprocal lattice, and double diffraction, and their significance in formation and interpretation of electron micrograph images and electron diffraction patterns. Some knowledge of stereographic projections and their manipulations is also desirable; Barrett [*10*] is a good reference.

The simplest case is that of the diffraction pattern from a single, fully annealed crystal. Even here, in the presence of one-to-several strong diffracted beams, the phenomenon of double diffraction may complicate analyses in the presence of second-phase regions, or for noncubic structures. Also, relaxation of the Bragg condition for diffraction from very thin portions of a foil specimen, and local lattice bending (especially in deformed crystals) may result in presence of unexpected spots and thus further complexity in indexing of the electron diffraction pattern. Simultaneous appearance of diffraction patterns from two or more grains, or from a grain and its twin, may also complicate the analysis. (Here a twin may be considered as a second grain, but with a specific orientation relative to the matrix.) The two grain (or grain-twin) condition generally can be recognized, and the selected area aperture of the electron microscope can be positioned successively to obtain a diffraction pattern from each single crystal region. Specific known twin-orientation relationships can be helpful in unscrambling superimposed diffraction patterns from twin-containing regions.

During photographing a thin foil electron micrograph and the corresponding diffraction pattern in the TEM, the two following procedures may aid subsequent diffraction analysis: (1) The TEM beam-stopper may be used, then removed during the final few seconds of the exposure to produce a sharp, clear spot for the undiffracted beam on the diffraction pattern. (2) Similarly, the corresponding "selected area" of the foil specimen (from which the diffraction pattern originated) may be indicated in the electron micrograph by superimposing (for a small fraction of the total exposure) a faint image of the selected area aperture, as it was positioned to obtain the diffraction pattern being analyzed.

In the stepwise procedure outlined next, it is assumed one has obtained a suitable diffraction pattern from an area of interest appearing in a thin foil electron micrograph which exhibits good diffraction contrast. For satisfactory analysis, the pattern generally should contain one strong diffraction spot (in addition to the undiffracted beam, that is, the "two-beam" condition), and must contain a number of additional spots. The latter should preferably total eight or more, not all lying in a single straight line, and preferably lying along three or more nonparallel straight lines through the undiffracted beam spot, as shown in Fig. 4.

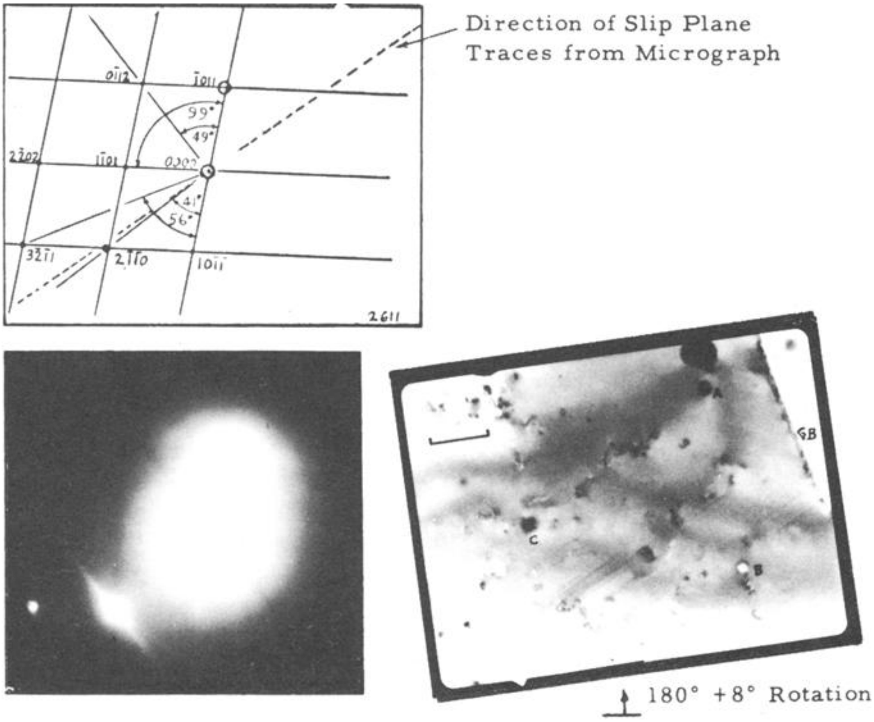
For convenience, standard contact-print orientation has been used in this procedure for both micrograph and diffraction pattern, that is, both are viewed with emulsion side of the negative away from the observer. Many electron microscopists prefer to use the opposite orientation which inherently provides better accuracy in tracing the diffraction pattern; however, in this case a contact printer cannot be used to make working prints of the micrograph and its diffraction pattern. An enlarger is required, and the negative must be inserted "upside down," that is, with emulsion side up. Accuracy using the orientation described here has been satisfactory. Whichever convention is selected, it must be used consistently.

4.7 Steps in the Solution of a Selected Area Spot Electron Diffraction Pattern of a Thin Foil Specimen

A. The diffraction pattern is carefully traced with a sharp pencil from the negative onto a piece of Mylar tracing film (or tracing paper), maintaining contact-print orientation (see preceding paragraph). This requires care to minimize parallax effects. The edges of the exposed area of the negative, including any indexing notches, should be carefully marked with short lines on

Spot No.	Relative Intensity	Multiplicity	r, mm.	(r/r_1)	Best Fit to (1/d) Ratio Tables Plane	 (r/r_1)
1	A, D, E	3	14.1	1.0	$10\bar{1}1$	1.0
2	G	1	18.4	1.31	$10\bar{1}2$	1.30
3	B	1	21.3	1.51	$11\bar{2}0$	1.52
4	F	1	28.3	2.01	$20\bar{2}2$	2.00
5	C	1	33.7	2.39	$21\bar{3}1$	2.37

Note: Angles from stereogram corresponding to those of diffraction pattern below, top to bottom, are: 99°, 49°, 40 1/2°, and 56 1/2°. Thus both 1/d-ratio and angular agreements are excellent.



Direction of Slip Plane Traces from Micrograph

180° +8° Rotation

FIG. 4—*Sample diffraction analysis worksheet with solution of pattern according to method of Part II (beryllium specimen E8K16).*

the tracing, so that for future checking the tracing can again be positioned on the negative in correct registry. The strong back illumination of a light box (a photo contact printer makes a powerful light box) may be needed to see the weakest diffraction spots. Tracing film and negative are held down with pressure sensitive tape. Tracing directly from the negative assures that the maximum number of diffraction spots are available for use in solving the pattern. Loss of significant weak spots often occurs when working from a positive print of the pattern, due to limited photographic latitude of the paper. It has proved helpful to indicate on the tracing the relative intensity of the diffraction spots on the negative, by size of circles or intensity of pencil dots (see Fig. 4).

B. The diffraction pattern tracing, the contact print of the diffraction pattern, and the corresponding electron micrograph print are attached in a compact arrangement to a worksheet, in correct relative orientation (Fig. 4). Here one must allow for the 180-deg image rotation inversion relative to the diffraction pattern, which occurs for each image forming inversion (crossover) in the electron microscope[3]. The image must be further rotated relative to the diffraction pattern to correct for the magnification-dependent rotation of the image (relative to the diffraction pattern) resulting from the spiral motion of the electrons through the magnetic lens fields. The required angle of rotation for each lens combination and magnification is determined from a rotation calibration, as outlined in Part I of this procedure.

C. The indexing of the diffraction pattern from this point can follow the procedure of Part I for spot patterns, Sections 4.4.1 and 4.4.3. The calibration of K versus OL current (Section 4.4.1C) was not used when the worksheet, shown in Fig. 4, was prepared. An alternate approach was used to compensate for variations in specimen position and consequently of OL current and diffraction-pattern size: ratios of radial measurements (r_x/r_1, or $(1/d_x)/(1/d_1)$) of the diffraction patterns were utilized in place of K (see also Tables 2 and 3).

D. After the diffraction pattern has been indexed by the procedure of Part I, a standard stereographic projection is used which has been prepared previously with pole locations only. This is on tracing paper, with pole spots but without their indices labelled.[4] It is attached to a fixture, centered over a rotatable Wulff net, for example as shown in Figs. 5, 6, and 7. A corresponding fully indexed standard projection is also at hand for reference, but it has been found much simpler to use the unindexed projection for the analysis and rotations. The tentatively indexed reflecting plane poles (from the diffraction pattern tracing) are then marked on the unindexed projection, that is, circled and labeled with the tentative indices on the tracing paper. If the indexing has been done

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[4] One method of preparing such stereographic projections which does not require special equipment other than small homemade punch, is to lay out the projection on Mylar tracing film, punch out the spots, then use this as a stencil, placing each piece of tracing paper under it and spraying with an aerosol can of black enamel.

TABLE 2–*Relative reciprocal lattice spacings for face centered cubic lattices* (1/d *ratios*).

N	*hkl*	111	200	220	311	222	400	331	420	422	333 511	440	531
3	111	1											
4	200	1.15	1										
8	220	1.63	1.41	1									
11	311	1.91	1.66	1.17	1								
12	222	2.00	1.73	1.22	1.04	1							
16	400	2.31	2.00	1.41	1.21	1.15	1						
19	331	2.52	2.18	1.54	1.31	1.26	1.09	1					
20	420	2.58	2.24	1.58	1.35	1.29	1.12	1.03	1				
24	422	2.83	2.45	1.73	1.48	1.41	1.22	1.12	1.10	1			
27	333, 511	3.00	2.60	1.84	1.57	1.50	1.30	1.19	1.16	1.06	1		
32	440	3.27	2.83	2.00	1.71	1.63	1.41	1.30	1.26	1.15	1.09	1	
35	531	3.42	2.96	2.09	1.78	1.71	1.48	1.36	1.32	1.21	1.14	1.05	1
36	600, 442	3.46	3.00	2.12	1.81	1.73	1.50	1.38	1.34	1.22	1.15	1.06	1.01
40	620	3.65	3.16	2.24	1.91	1.83	1.58	1.45	1.41	1.29	1.22	1.12	1.07
43	533	3.79	3.28	2.32	1.98	1.89	1.64	1.50	1.47	1.34	1.26	1.16	1.11
44	622	3.83	3.32	2.35	2.00	1.91	1.66	1.52	1.48	1.35	1.28	1.17	1.12
48	444	4.00	3.46	2.45	2.09	2.00	1.73	1.59	1.55	1.41	1.33	1.22	1.17
51	711, 511	4.12	3.57	2.52	2.15	2.06	1.79	1.64	1.60	1.46	1.37	1.26	1.21
52	640	4.16	3.61	2.55	2.17	2.08	1.80	1.65	1.61	1.47	1.39	1.27	1.22
56	642	4.32	3.74	2.65	2.26	2.16	1.87	1.72	1.67	1.53	1.45	1.32	1.26
59	731, 553	4.43	3.84	2.72	2.32	2.22	1.92	1.76	1.72	1.57	1.48	1.36	1.30
64	800	4.62	4.00	2.83	2.41	2.31	2.00	1.84	1.79	1.63	1.54	1.41	1.35
67	733	4.73	4.09	2.89	2.47	2.36	2.05	1.88	1.87	1.67	1.58	1.45	1.38
68	820, 644	4.76	4.12	2.92	2.49	2.38	2.06	1.89	1.84	1.68	1.59	1.46	1.39
72	822, 660	4.90	4.24	3.00	2.56	2.45	2.12	1.95	1.90	1.73	1.63	1.50	1.43
75	555, 751	5.00	4.33	3.06	2.61	2.50	2.17	1.99	1.94	1.77	1.67	1.53	1.46
76	662	5.03	4.36	3.08	2.63	2.52	2.18	2.00	1.95	1.78	1.68	1.54	1.47
80	840	5.16	4.47	3.16	2.70	2.58	2.24	2.05	2.00	1.83	1.72	1.58	1.51

correctly, the labeled poles on the stereographic projection can be made to lie along or close to a common great circle, by rotating the Wulff net beneath them about its center. (The Wulff net is then left in this rotated orientation for Step 4.7E.) If this cannot be done, the reason must be found, and the indexing must be corrected. For an explanation of stereographic projection manipulation, see Ref *5* or *10*.

E. The foregoing great circle test is one check of correct indexing of the diffraction pattern tracing; it is the equivalent of the zone axis requirement of Part I or Ref *11*. Another check is that of rational indices[*11*], which requires that corresponding digits of the indices of spots lying along a common "grid" line of the diffraction pattern tracing must increase or decrease by a constant, whole number, algebraic increment, or remain constant, as one moves along any grid line, assuming equal spacing between successive spots. If this requirement is not met, the indexing must again be corrected accordingly. For example, along

TABLE 3–*Relative reciprocal lattice spacings for body centered cubic lattices* (l/d *ratios*).

hkl	110	200	211	310	222	321	411	420	332	510 431	521	530 433
110	1											
200	1.415	1										
211	1.73	1.225	1									
220	2.00	1.415	1.155									
310	2.235	1.58	1.29	1								
222	2.45	1.73	1.415	1.095	1							
321	2.645	1.87	1.53	1.185	1.08	1						
400	2.83	2.00	1.63	1.265	1.155	1.07						
411, 330	3.00	2.12	1.73	1.34	1.225	1.135	1					
420	3.16	2.235	1.825	1.415	1.29	1.195	1.055	1				
332	3.315	2.345	1.915	1.485	1.355	1.255	1.105	1.05	1			
422	3.465	2.45	2.00	1.55	1.415	1.31	1.155	1.095	1.045			
510, 431	3.605	2.55	2.08	1.61	1.47	1.365	1.20	1.14	1.09	1		
521	3.875	2.74	2.235	1.73	1.58	1.465	1.29	1.245	1.17	1.075	1	
440	4.00	2.83	2.31	1.79	1.63	1.51	1.335	1.265	1.21	1.11	1.035	
530, 433	4.125	2.915	2.38	1.845	1.685	1.56	1.375	1.305	1.245	1.145	1.065	1
600, 442	4.245	3.00	2.45	1.895	1.73	1.605	1.415	1.34	1.28	1.18	1.095	1.03
611, 532	4.36	3.08	2.52	1.95	1.78	1.65	1.455	1.38	1.315	1.21	1.125	1.06
620	4.47	3.16	2.58	2.00	1.825	1.69	1.49	1.415	1.35	1.24	1.155	1.085
541	4.585	3.24	2.645	2.05	1.87	1.73	1.53	1.45	1.38	1.27	1.185	1.11
622	4.69	3.315	2.71	2.10	1.915	1.77	1.565	1.485	1.415	1.30	1.21	1.135
631	4.795	3.39	2.77	2.145	1.955	1.815	1.60	1.515	1.445	1.33	1.24	1.16
444	4.90	3.465	2.83	2.19	2.00	1.85	1.635	1.55	1.48	1.36	1.265	1.185
710,550,543	5.00	3.535	2.89	2.235	2.04	1.89	1.665	1.58	1.51	1.385	1.29	1.21
640	5.10	3.605	2.94	2.28	2.08	1.925	1.70	1.61	1.54	1.415	1.315	1.235
721,633,552	5.195	3.675	3.00	2.325	2.12	1.955	1.73	1.645	1.57	1.44	1.34	1.26
642	5.29	3.74	3.055	2.365	2.16	2.00	1.765	1.675	1.595	1.47	1.365	1.285
730	5.385	3.81	3.11	2.41	2.20	2.035	1.795	1.705	1.625	1.495	1.39	1.305

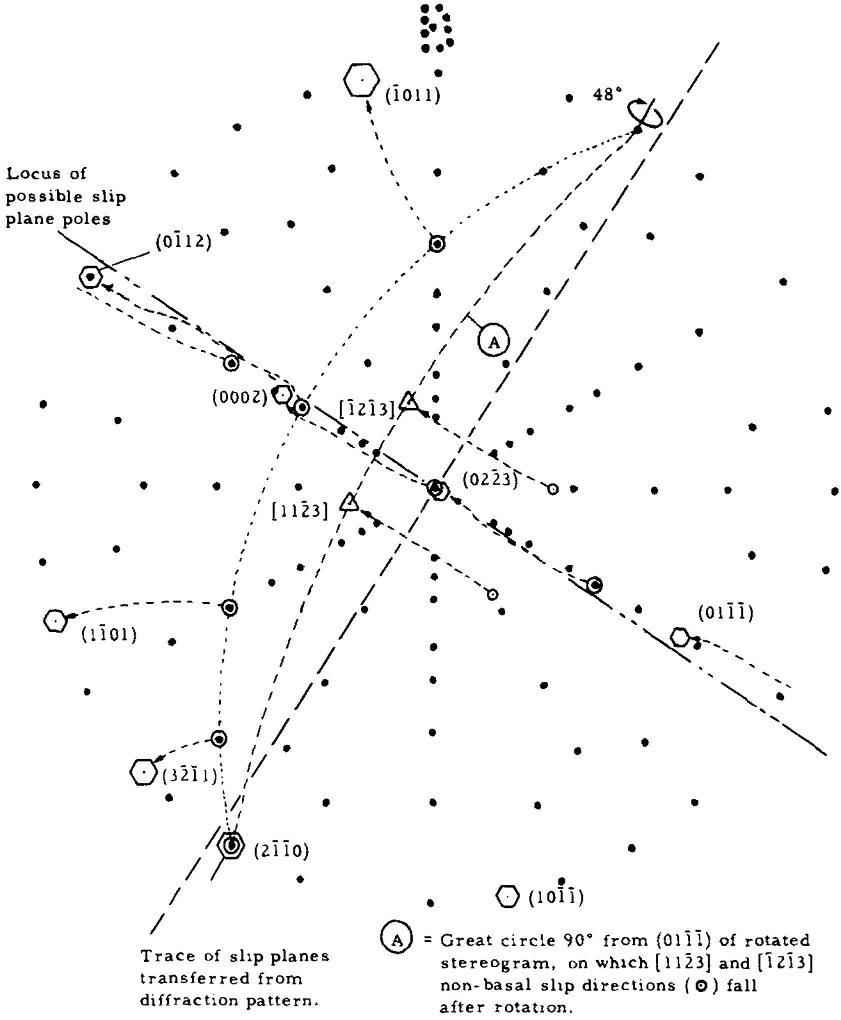


FIG. 5–*Stereographic projection for sample analysis of Fig. 4, prepared using unindexed standard projection on tracing paper, showing both standard and rotated orientation, with rotations indicated.*

the lower "horizontal grid" line of Fig. 4, where the indices are $(3\bar{2}\bar{1}1)$, $(2\bar{1}\bar{1}0)$, and $(10\bar{1}\bar{1})$, the first and last indices progressively decrease by one, the second increases, and the third remains constant.

F. The stereographic projection is rotated from the standard projection orientation, by moving each of the diffraction plane poles along its latitude line of the Wulff net (each pole being moved the same number of longitude degrees),

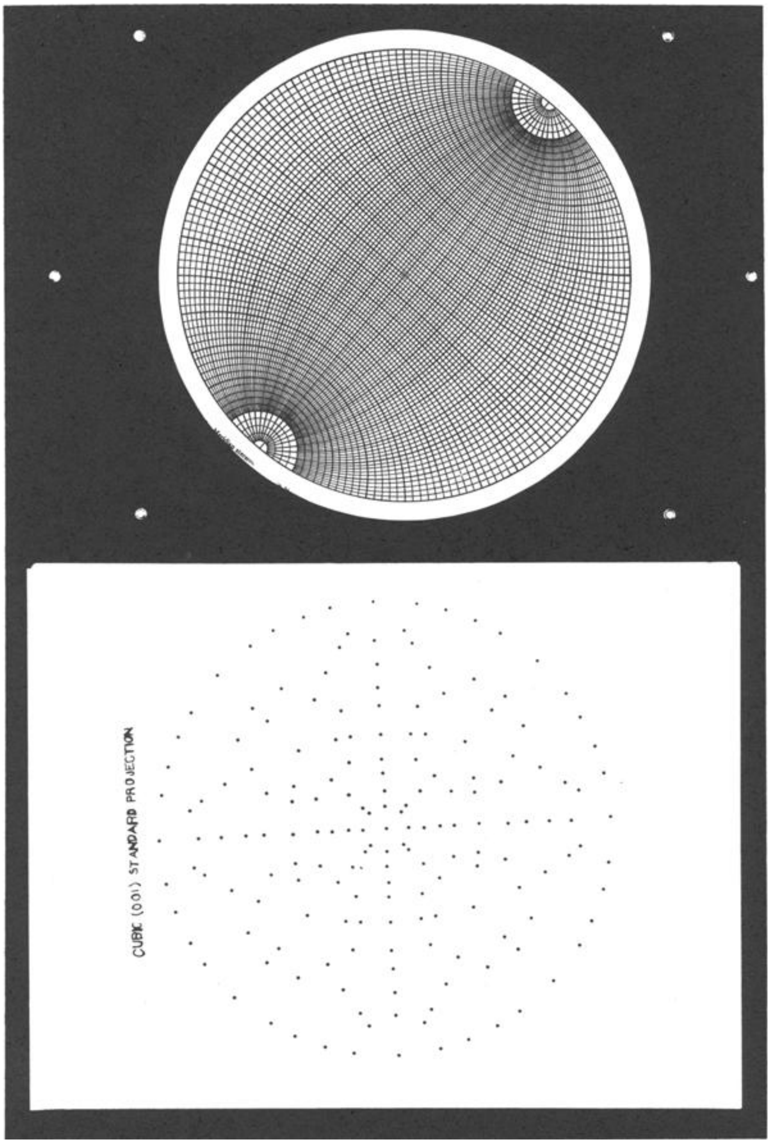


FIG. 6—*Photograph of stereographic projection/Wulff net fixture and of unindexed cubic 001 projection which is taped to outer, nonrotating portion of fixture, centered over rotable Wulff net.*

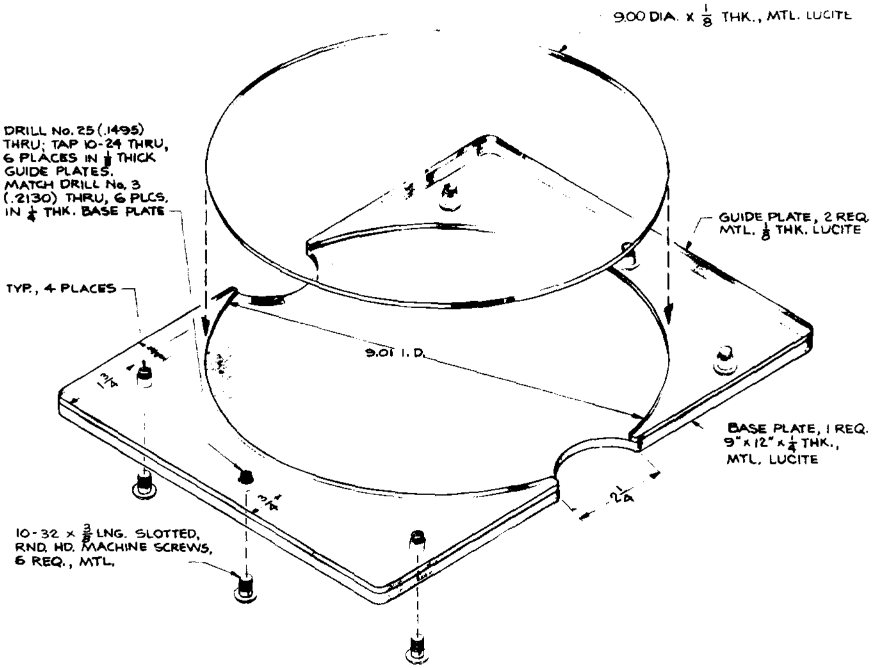


FIG. 7–*Fixture for 18-cm stereographic projection and Wulff net.*

to bring the poles corresponding to the indexed diffraction spots to (or close to) the outside periphery of the projection (Fig. 5). The rotated projection then corresponds fully to the orientation of the crystal in the TEM foil specimen which produced the diffraction pattern. That is, the center of the rotated projection coincides with the axis of the TEM incident electron beam. In the rotated stereogram, the angle subtended at the center of the stereogram by the poles of two diffracting planes must equal the angle subtended on the diffraction pattern tracing at the central (undiffracted) spot by the two corresponding diffraction spots. This is a rigid requirement, and experience has indicated that the angular agreement should be within 2 deg.

G. Traces or projected directions of features of interest in the electron micrograph may now be transferred to the indexed diffraction pattern tracing (on the worksheet described earlier, Fig. 4). A line is drawn through the central spot of the tracing parallel to the trace or direction of interest in the micrograph. By the angular considerations of 4.7E this direction may be transferred to the rotated stereogram as a line through the center (Fig. 5). If this line corresponds to a trace such as that of a slip plane made by a moving dislocation, the pole of the slip plane must lie (within the limits of accuracy of the technique, in this case, approximately 3 deg) along a diametral great circle of the stereogram at 90 deg to the line corresponding to the trace. In the case of a projected direction in the micrograph such as that of a dislocation line, the crystallographic direction of the feature must be represented by a direction on the stereogram lying at some position along the diametral line transferred from micrograph to diffraction pattern tracing, then to stereogram.

H. For cubic crystals, the pole of a plane and the direction having the same indices coincide in the standard stereographic projection. However, it must be remembered that the poles of the standard projection for a hexagonal (or other noncubic) metal represent planes which are not normal to directions in the crystal having the same indices. Therefore, points on the stereogram corresponding to crystallographic directions vary in their positions relative to poles of planes having the same indices, depending on the specific *c/a* axial ratio of the (hexagonal or tetragonal) crystal in question. The angle between the *c*-direction and any low indices direction is readily calculated from simple geometric considerations, using the *c/a* axial ratio for the crystal under study.

APPENDIX 4.1

Alternate Method for Calculating the Electron Microscope Camera Constant

Another method of calculating the camera constant (K) is based on the equation

$$K = L\lambda \tag{7}$$

But this applies only to no-lens diffraction, that is, all the image lenses must be turned off. In this case L is the distance from the specimen to the photographic plate in millimeters (and can be obtained from the microscope specifications or from a schematic of the column itself), and λ is the electron beam wavelength in angstroms readily available in references on electron microscopy[*1,3*]. If this method is applied to selected area diffraction, then L is actually the effective length, because it varies with strength of the objective and magnification lenses and with the exact position of the specimen along the microscope axis.

The wavelength λ can be calculated from the deBroglie equation $\lambda = h/(mv)$ but with relativistic corrections to account for the change in mass with velocity as follows:

$$\lambda = \frac{h}{\sqrt{(m + m_o)Ee}} \tag{8}$$

where h is Plank's constant (6.624×10^{-27} erg/s), m is the mass of a moving electron $m = \dfrac{m_o}{\sqrt{1 - \mu 2/_c 2}}$, μ is its velocity, and c is the velocity of light), m_o is the rest mass (9.1066 X 10^{-28} g), E is the accelerating potential, and e is the electronic charge (1.6020 X 10^{-2} *emu*). A more common form is:

$$\lambda = \frac{h}{\left(2m_oEe\left(1 + \frac{Ee}{2m_oc^2}\right)\right)^{1/2}} \qquad (9)$$

or further simplifying by combining constants:

$$\lambda = \frac{12.26}{E^{1/2}(1 + 0.9788 \times 10^{-6}E)^{1/2}} \qquad (10)$$

where E is the accelerating potential. Wavelengths for some accelerating potentials are listed in Table 4, to show decreasing wavelength with an increase in accelerating potential and also to illustrate the importance of calculating wavelengths of higher energy beams taking into account the relativistic correction.

It may be significant to note here that the higher the accelerating potential, the shorter the wavelength, thus the greater the theoretical resolving power.

APPENDIX 4.2

Equations for Cubic, Hexagonal, and Tetragonal Systems Relating Miller Indices to Interplanar Spacing *d*, Lattice Parameter *a*, and Radial Distance of Diffraction Spots *r*

1. *Cubic Crystal System*

$$r^2 \propto (h^2 + k^2 + l^2) \qquad (11)$$

TABLE 4–*Electron beam wavelength as a function of accelerating potential.*

Accelerating Potential E, kV	Corrected Wavelength λ, A	Uncorrected Wavelength, $\lambda = \frac{h}{\sqrt{2m\,Ee}}$
10	0.1220	0.1225
50	0.0536	0.0548
60	0.0487	0.0500
80	0.0418	0.0433
100	0.0370	0.0387
160	0.0280	0.0306
200	0.0251	0.0274
300	0.0197	0.0224
500	0.0142	0.0173
800	0.0103	0.0137
1000	0.0087	0.0122

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} \qquad (12)$$

2. *Hexagonal Crystal System*

$$r \alpha (h^2 + hk + k^2) + \left(\frac{l}{c}\right)^2 \qquad (13)$$

For the condition when the basal plane is normal to the electron beam, $l^2/c^2 = 0$.

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \left(\frac{l}{c}\right)^2 \qquad (14)$$

3. *Tetragonal Crystal System*

$$r^2 \alpha (h^2 + k^2) + \left(\frac{l}{c}\right)^2$$

For the condition when the *c* parameter is parallel to the electron beam, $l^2/c^2 = 0$.

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \qquad (15)$$

APPENDIX 4.3

Example of a Stepwise Solution to a Problem of Identification of Unknown Precipitates in an Extraction Replica of an Iron-Columbium Alloy

A specimen of about 1 cm^3 was mounted in bakelite and metallographically polished to Linde B, with the final polish-etch procedure repeated three times to remove the disturbed metal. The specimen was etched in saturated picral for 15 s and then coated with a carbon film in a vacuum evaporator. A carbon tip 1/16 in. in diameter and 3/16 in. in length was evaporated on the specimen 10 cm from the source. The coated surface was scribed lightly into 2 mm squares. The specimen was then immersed in saturated picral etchant for 1/2 h. In this time the etchant penetrated the carbon film and dissolved the matrix, releasing the carbon film or appearing to form bubbles under the film. The specimen was then rinsed very carefully but thoroughly with methyl alcohol and slowly immersed in a dish of distilled water. The surface tension of the water caused the carbon film squares to float on the surface. The small squares of carbon extraction replicas were captured on 200 mesh and 75 mesh copper grids, carefully blotted on absorbent paper to dry, and placed in the electron microscope.

Examination revealed rows of very fine precipitates 180 to 600 angstroms in diameter, a thin flakelike grain boundary phase and a few large disk-shaped particles about 1/2 μm in diameter in the matrix, as shown in Fig. 8, *a*, *b*, and *c*, respectively. Attempts to get single crystal spot diffraction patterns from the fine row precipitate were unsuccessful because even though a small 3-μm-diameter selected area diffraction aperture was tried, the individual precipitates failed to yield enough spots to index the pattern for identification. However, by using a 30 or 50-μm-diameter selected area diffraction aperture, enough of the fine precipitates were in the field to yield a sharp ring pattern, as can be seen in Fig. 8*a*. The 30-μm selected area diffraction aperture is shown on the particle in Fig. 8*b*, with the resulting diffraction pattern. A dark field image and pattern of a disk-shaped particle are shown in Fig. 8*c*.

Measurements and results from following the step-by-step outline in the text (Part I) are shown in Table 5 for the first five innermost rings. The microscope camera constant (K) was determined from measuring a ring pattern of an evaporated gold film and the calculated K using Eq 1, averaged to be 19.35 mm Å for this objective current and accelerating voltage. After calculating the d values ($d = K/r$) from the ring pattern of two different plates, the ASTM Powder Diffraction File Index was examined to find the nearest corresponding sets of d values, so the card for each was removed and examined. From the known composition of the alloy, the compounds scandium nitride, tantalum carbide, and titanium deuterium were discounted leaving columbium carbide and columbium nitride oxide as the possible precipitate. The pattern was identified as columbium carbide (CbC)[*9*] because the d values more precisely corresponded to CbC, and, with only 0.001 percent nitrogen known to be present in the alloy, it can be safely concluded that the precipitates were not oxidized columbium nitrides.

In order to identify the large, thin flakelike particles that seemed to have formed in grain boundaries, a 30-μm-diameter selected area diffraction aperture was used to obtain a single crystal spot pattern from a single particle. Following the step-by-step procedure outlined in Part I of the procedure for indexing single particle spot patterns, the results, shown in Table 6, were obtained.

The assumed hkl values from Table 6 all satisfy the condition for the fcc rule as given in 4.4.3G of the text; that is, h, k, and l must be all odd or all even, so the structure is assumed to be fcc. The spots were measured directly from the plate, but the angles between the spots were measured on a print of the pattern enlarged three times. Straight lines were drawn through the spots, and the angles were measured with a protractor. The measured angles and real angles taken from Cullity[*5*] are shown in Table 7, and all measured values agree with the real values within 2 deg, as suggested in Part II, 4.7F.

TABLE 5—*Ring measurements from Plate No. 17417, fine row precipitates.*

Ring	Diameter, mm	Radius, mm	d(Å) = K/r	Diffraction Card[a] d Values	
			No. 17417	CbC	Cb-N-O
1	15	7.5	2.580	2.58	2.57
2	17.3	8.65	2.237	2.23	2.20
3	24.5	12.25	1.579	1.580	1.56
4	28.65	14.325	1.350	1.348	1.33
5	30.00	15.00	1.290	1.290	1.28

[a] ASTM Index File No. 10-181 = CbC, and 12-256 = Cb-N-O.

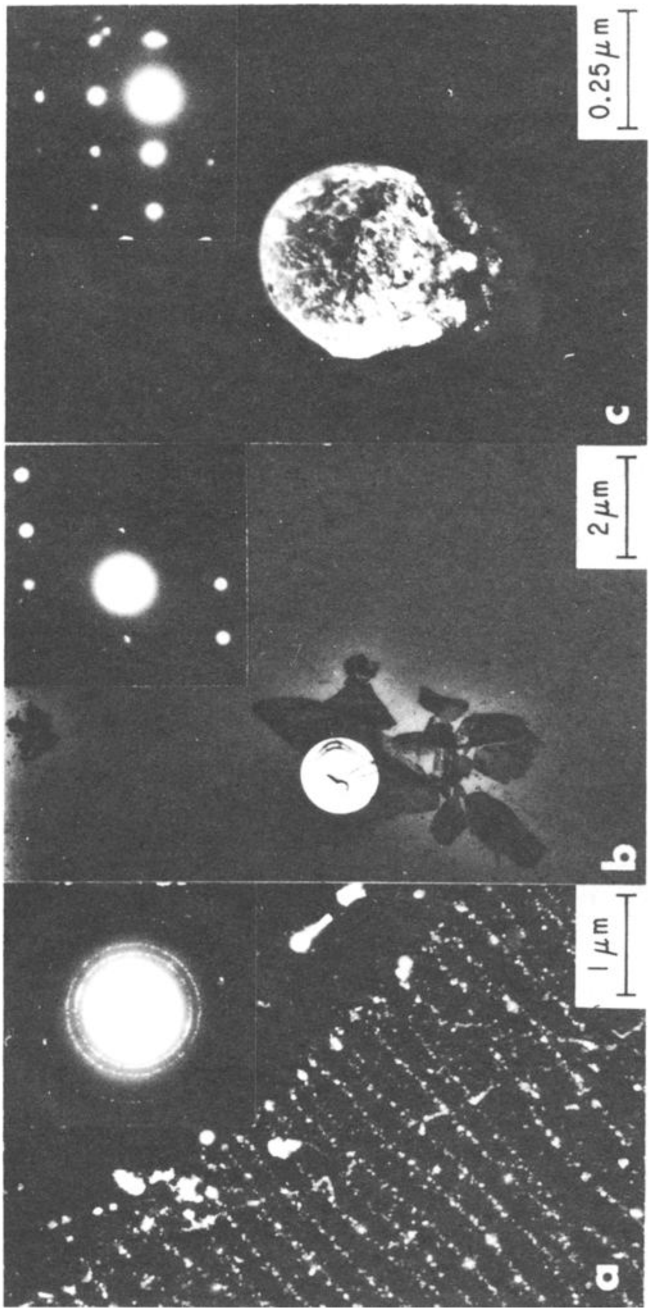


FIG. 8—*Carbon extraction replica of 3 types of precipitates and patterns from an iron-columbium alloy.*

TABLE 6–*Measured radius values from Plate No. 17415, thin flakelike particle.*

Spot	Radius, r(mm)	r^2 (mm)	Divide by r_1^2	Times 3	$(h^2+k^2+l^2)$	hkl	$K/r = d$	Actual d^a
1	7.42	55.06	1	3	3	111	2.587	2.58
2	12.33	152.03	2.761	8.28	8	220	1.557	1.580
3	14.46	209.09	3.796	11.39	11	311	1.327	1.348
4	19.43	377.52	6.857	20.57	20	420	0.9881	0.999

[a] ASTM Index File No. 10-181 = CbC.

The d values were calculated using Eq 8 and are shown in Table 6. The assumed Miller indices from Tables 6 and 7 were assigned to the corresponding spots, as shown in Fig. 9.

As explained in Step 4.4.3J of the text, a check at this point should be made because although the type plane may be correct, the sign may not be. Vector addition of spots 1 and 2 revealed that spot 3 was not correct. The procedure then followed was:

1. Spot 1 was assigned (111).
2. Knowing spot 2 is type {220} and 90 deg from spot 1, a standard (001) cubic projection was used to find a type {220} plane on the 90 deg great circle from the (111) pole. It was found that the $(0\bar{1}1)$ and $(\bar{1}10)$ poles are 90 deg from (111), so spot 2 was assigned the $(\bar{1}10)$ or $(\bar{2}20)$. Then by vector addition of spots 1 and 2, spot 3 was found to be $(\bar{1}31)$, as shown in Fig. 10 with the correctly indexed spots. By assigning spot 5, $2(h_1k_1l_1) = 2\,(111) = (222)$, spot 4 was determined by vector addition of spots 5 and 2. Knowing these 5 spots to be correctly indexed, step 4.4.3K of Part I was followed to index the diametrically opposite spots with a change in the sign of the Miller indices. The remaining spots were indexed by vector addition and labelled, as shown in Fig. 10.

The lattice parameter was calculated from Eq 12, $a = \sqrt{d^2(h^2+k^2+l^2)}$ for each of the 4 spots, and varied as follows: 4.48, 4.42, 4.41, and 4.43 for an average of 4.43. From the measured and calculated d values and lattice parameter it was concluded that the large thin grain boundary particles were also columbium carbides (lattice parameter a = 4.465 Å). The orientation or zone

TABLE 7–*Measured angles from Plate 17415, thin flakelike particle.*

Angle Between Spots	hkl Planes	Measured Degrees	Actual	Degrees from Cullity[5]
1–2	111–220	88	90	111–110
1–3	111–311	58	58.5	111–311
1–4	111–420	39	39.2	111–210
2–3	220–311	30	31.5	110–311
2–4	220–420	49	50.8	110–210
3–4	311–420	19	19.3	311–210

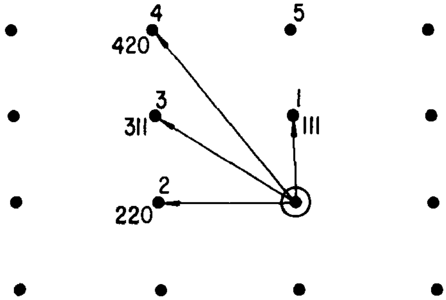


FIG. 9–*Selected area diffraction pattern from thin filmlike particle.*

axis of the pattern was calculated using Eq 13 for the (111) and ($\bar{2}20$) spots, that is, by:

$$\begin{aligned} k_1 l_2 - l_1 k_2 &= u \qquad (1)(0) - (1)(2) = \bar{2} = u \\ l_1 h_2 - h_1 l_2 &= v \qquad (1)(\bar{2}) - (1)(0) = \bar{2} = v \\ h_1 k_2 - k_1 h_2 &= w \qquad (1)(2) - (1)(\bar{2}) = 4 = w \end{aligned} \tag{16}$$

cross multiplying the indices of any two spots. As a check for the correct zone axis, Eq 14 was used for spot (042).

$$\begin{gathered} hu + kv + lw = 0 \\ (0)(\bar{2}) + (4)(\bar{2}) + (2)(4) = 0 \end{gathered} \tag{17}$$

Repeating Eq 14 with spot ($\bar{1}31$) also equalled zero. Therefore, it is reasonable to assume that the zone axis $[uvw]$ of the pattern or orientation of the particle is ($\bar{2}\bar{2}4$) or ($\bar{1}\bar{1}2$).

Also present in the extraction replica were large thick disklike particles about ½ μm in diameter. Most of these particles were too thick to obtain a satisfactory

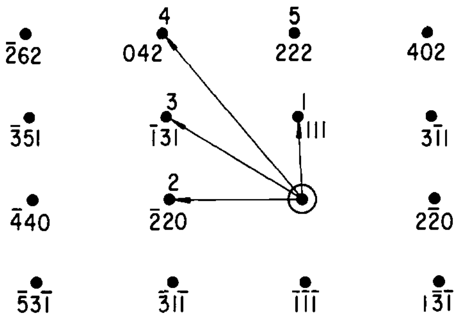


FIG. 10–*Correctly labeled pattern from thin filmlike particle.*

TABLE 8–*Measured radius values from Plate No. 17427, thick disklike particle.*

Spot	Radius, r (mm)	r^2 (mm)	Divide by r_1^2	Times 1	$(h^2 + k^2 + l^2)$	*hkl*	$K/r = d$	Actual d^a
1	7.3	53.2	1	1	1	100	2.616	2.612
2	7.3	53.2	1	1	1	100	2.616	2.612
3	10.25	105.06	1.97	2	2	110	1.863	1.847
4	16.25	264.06	4.96	5	5	210	1.175	1.168

^{a} ASTM Index File No. 6-0518 = α-manganese sulfide.

TABLE 9–*Measured angles from Plate No. 17427, thick disklike particle.*

Angle Between Spots	*hkl* Planes	Measured Degrees	Actual	Degrees from Cullity [*5*]
1–2	200–200	89	90	100–100
1–3	200–220	46	45	100–110
1–4	200–420	64	63.4	100–210
2–4	200–420	26	26.6	100–210
3–4	220–420	18	18.4	110–210

diffraction pattern, but a few were thin enough because of having been polished away mechanically prior to making the extraction replica. A diffraction pattern from one of these particles was analyzed and indexed using steps 4.4.3C through 4.4.3L in Part I, with the results listed in Tables 8 and 9.

The lattice parameter (*a*) was calculated using Eq 12 for each of the 4 measured spots, and the results were 5.23, 5.23, 5.27, and 5.25 for an average of 5.25 Å. The sketch of the correctly indexed pattern is shown in Fig. 11.

Knowing the *d* values and lattice parameter, the ASTM Powder Diffraction File Index revealed five possible compounds that very nearly corresponded to the calculated *d* values. However, knowing the chemical composition of the original material made it easy to discount four of these, leaving the compound alpha manganese sulfide as the identification of the particle. The calculated lattice parameter was 5.25 Å, corresponding to the index value of 5.224.

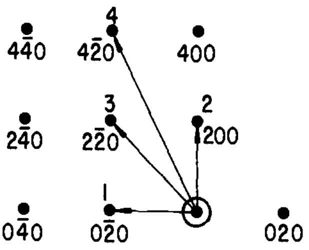


FIG. 11–*Correctly indexed pattern from thick disklike particle.*

The zone axis of the pattern or orientation of the particle was calculated using Eq 13 for (200) and $(0\bar{2}0)$, and was found to be $[00\bar{4}]$ or $[00\bar{1}]$.

All three phases in the extraction replica of a low alloy steel specimen are now identified as fine columbium carbide precipitate, large flake columbium carbide grain boundary particles, and large thick disklike α-manganese sulfide particles by using the step-by-step procedure outlined in Part I.

APPENDIX 4.4

Example of Identification and Determination of Orientation Relationship of Row Precipitates in a Low-Carbon, Vanadium Steel Thin Foil Specimen

The systematic study of the morphology characteristics (that is, size, shape, distribution, and orientation relationship with the matrix) of submicron size precipitates is necessarily restricted to electron microscopy. To determine the orientation relationship a further requirement is the application of TEM of thin foil specimens so that single crystal diffraction patterns are obtained for both the precipitate and the matrix. To index the diffraction pattern one must separate the precipitate and matrix reflections (spot patterns) by making use of the repeatability and symmetry of the respective patterns. The indexing then proceeds as for a typical single crystal pattern for which the distances from the center spot and the angles between reflections are measured and calculations are performed to determine the lattice plane and the zone axis of both the precipitate and matrix (as described in detail in the text, Part I, 4.4.3).

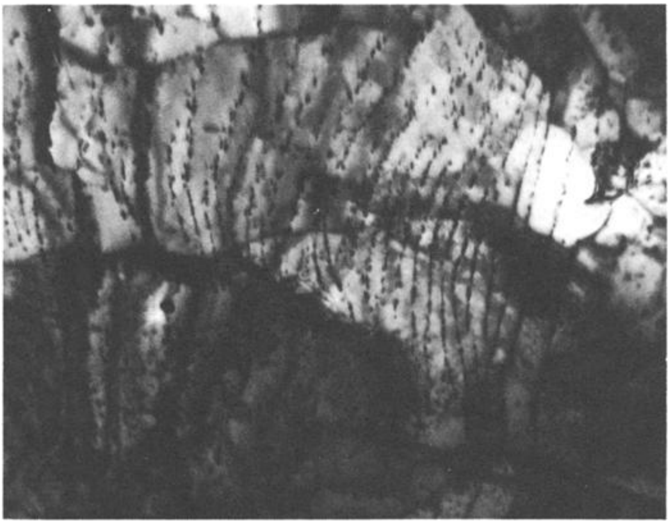
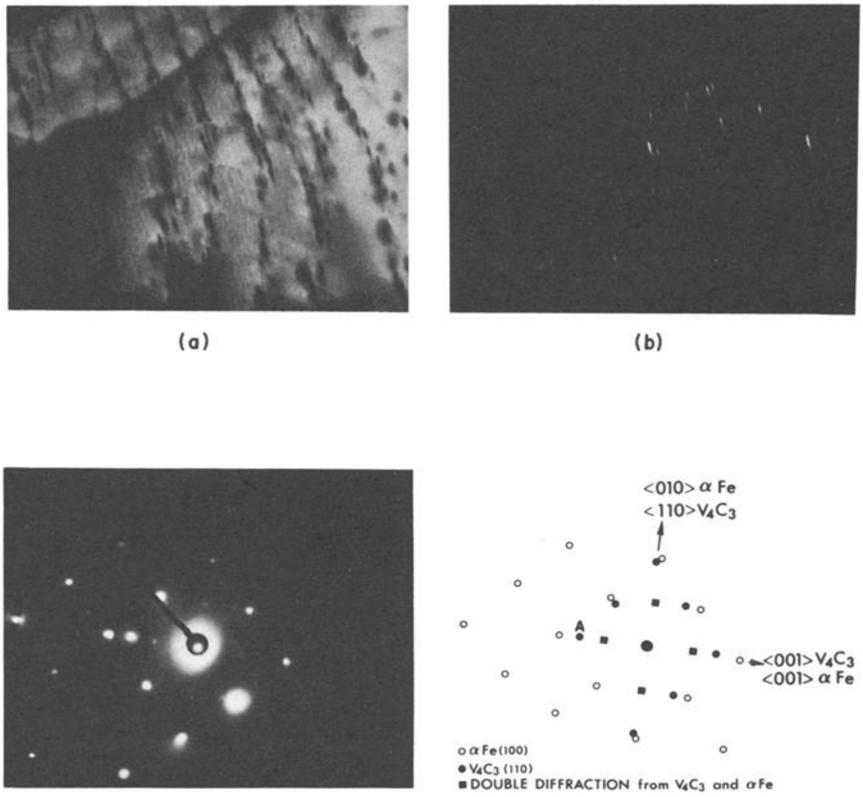


FIG. 12—*Bright field electron micrograph showing substructure and both row and matrix precipitates* (×*10 000*).

Complications due to double diffraction are considered in the following example where the relatively simple pattern due to vanadium carbide (V_4C_3) row precipitates in an α-iron matrix is indexed to reveal the orientation relationship for this particular precipitate/matrix combination.

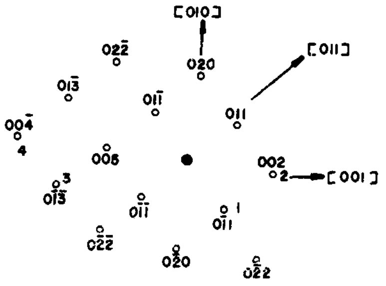
A thin foil was prepared from an 0.015-in.-thick wafer of the material using the standard jet electropolishing procedure and a 10 percent perchloric acetic acid solution. A bright field electron micrograph, representative of the substructure and both row and matrix precipitates, is shown in Fig. 12. To most easily identify the precipitate and the orientation relationships between the precipitate and the matrix, indexing was performed on a simple SAED pattern which was obtained through the use of the specimen tilt stage of the TEM. This procedure produced the multispot SAED pattern shown in Fig. 13*c*. To aid in



(a) (b)

(c) (d)

FIG. 13—*Orientation relationship of row precipitates:* (a) *bright field electron micrograph of row precipitates,* (b) *dark field of same area using the* (002) V_4C_3 *reflection to form the image,* ×*40 000,* (c) *SAED of* (a) *the objective aperture indicating the reflection used for* (b), (d) *schematic of* (c) *identifying the reflections.*

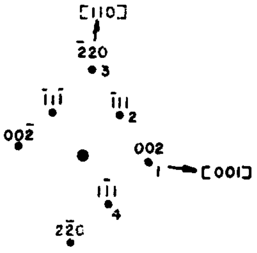


(100) α Fe Pattern

			α-Fe	
Spot	Radius, in.	$d = \frac{1.065}{R}$	hkl	d_{hkl}
1	0.52	2.050	110	2.027
2	0.74	1.442	200	1.433
3	1.16	0.903	310	0.906
4	1.52	0.702	400	0.721

Note: Camera constant = 1.065 Å in.

FIG. 14–*Indexing the α-iron portion of the SAED pattern shown in Fig. 13c.*



(110) V_4C_3 Pattern

			V_4C_3	
Spot	Radius, in.	$d = \frac{1.065}{R}$	hkl	d_{hkl}
1	0.55	1.940	200	2.065
2	0.45	2.370	111	2.385
3	0.73	1.463	220	1.460
4	0.44	2.420	111	2.385

Note: Camera constant = 1.065 Å in.

FIG. 15–*Indexing the V_4C_3 portion of the SAED pattern shown in Fig. 13c.*

distinguishing between the matrix and precipitate reflections, the objective aperture was used to produce the dark field image shown in Fig. 13*b*, thus indicating a definite precipitate originating reflection.

This reflection is represented by a closed circle and designated *A* in the schematic shown in Fig. 13*d*. Generating a periodic lattice network and looking for symmetry relationships, the remainder of the precipitate spot pattern is obtained as shown by the closed circles in Fig. 13*d*. The rather obvious matrix single crystal spot pattern is indicated by the open circles. Further support that these reflections are from the matrix may be obtained by moving the objective aperture over any of these strong reflections to provide a dark field image of the matrix in which the entire viewable area is in fluorescence. Those familiar with SAED patterns will easily recognize the matrix single crystal pattern as a (100) for a bcc crystal structure rotated approximately 45 deg from the horizontal. The details of indexing this portion of the pattern is summarized in Fig. 14. A similar procedure was followed for the precipitate originating reflections as summarized in Fig. 15.

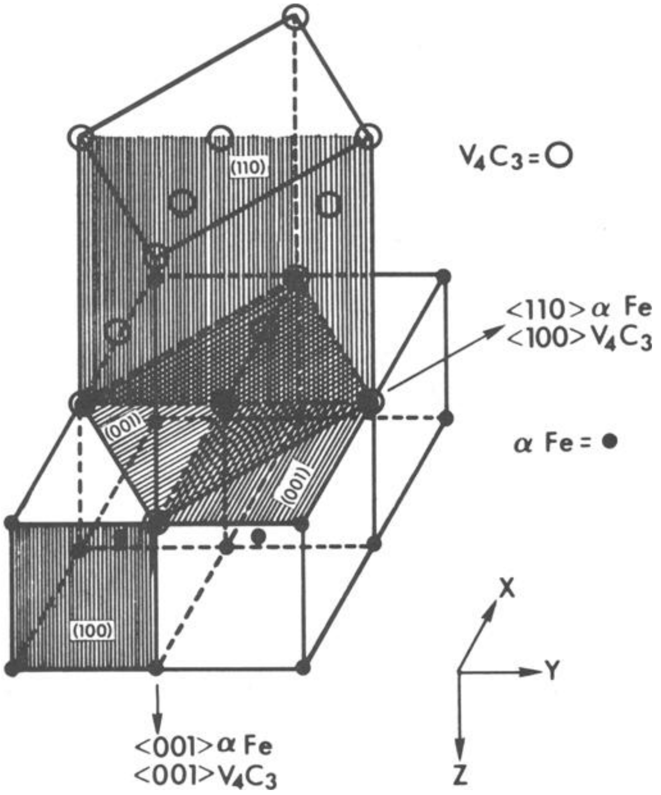


FIG. 16–*Schematic representation of the orientation relationship between the* V_4C_3 *row precipitates and the α-iron matrix.*

On the basis of the calculated *d* spacings, the precipitate was identified as V_4C_3 and the matrix as α-iron. Accordingly, by combining the determined lattice planes and zone axes for the precipitate and matrix, the orientation relationship was determined to be (100) α-iron//(110)V_4C_3, [001] α-iron//[001] V_4C_3. This atomic arrangement is shown schematically in Fig. 16.

One final consideration for the complete analysis of the SAED pattern is an explanation of the reflections indicated by the closed squares in Fig. 13*d*. These reflections are caused by double diffraction from the precipitate and matrix. The phenomenon of double diffraction is quite common when the two phases present (that is, precipitate and parent matrix) both produce strong diffraction patterns. Double diffraction simply arises when a diffracted ray from one set of planes ($h_1k_1l_1$ of spacing d_1, for example, from matrix or precipitate) is further diffracted by another set ($h_2k_2l_2$ of spacing d_2, for example, from precipitate or matrix). Because of the restrictions on the paths of these rays in crystal space, the corresponding extra reflections in reciprocal space are related to the singly diffracted reflections by simple vector mathematics (that is, $h_3 = h_1 \pm h_2$, $k_3 = k_1 \pm k_2$, $l_3 = l_1 \pm l_2$). Therefore, the extra spot pattern due to double diffraction will have a symmetry similar to the base pattern and can be distinguished generally by superimposing and aligning a tracing of the suspected double diffraction pattern with the base pattern.

In summary, the purpose of this example has been to illustrate a general approach to the indexing of a multispot diffraction pattern characteristic of a two-phase microstructure for which an orientation relationship existed between the precipitate and matrix phases.

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