

3.5. Preparation of specimens for electron diffraction and electron microscopy

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3.5.1. Ceramics and rock minerals

Transmission-electron-microscopy studies of ceramics and rocks require electron-transparent specimens in the form of flakes, profiled thin-foil discs, and evaporated films. These specimens are made from bulk ceramics and minerals by techniques that retain the structure and composition of the original sample. All three specimen types may be required for some studies of a single material. Fragments are made easily and are used extensively for diffraction analysis and for high-resolution structure imaging. Evaporated films are made for composition standards as well as for material process samples. Profiled thin-foil discs are most useful where direct comparison is required between the disc and the bulk sample from which it is made.

The thin-foil disc-shaped specimen fits directly in the specimen holder of the electron microscope. There is a tapered thin region at the centre of electron transparency and a thick rim for rigidity and support. One surface can be flat or both surfaces can be tapered as needed. Profiled specimens retain the microstructure of a bulk sample and can be prepared from any material. This type of specimen can be made from cross sections of multilayer materials as well as from parallel sections of multilayer materials. They are handled easily with vacuum tweezers, cleaned when necessary, and examined in the microscope repeatedly. The profiling of a disc specimen is achieved during ion thinning or by mechanical grinding, trepanning with an ultrasonic tool, grit blasting, or chemical dissolution prior to ion thinning. Thinned, insulating specimens should be coated with carbon to reduce electron-beam charging in the electron microscope. Specialized preparation techniques for ceramics have been described by many authors (Amelinckx, 1964; Bach, 1970; Barber, 1970; Butler & Hale, 1981; Drum, 1965; Goodhew, 1972, 1993; Hobbs, 1970; Hirsch, Howie, Nicholson, Pashley & Whelan, 1965; Thomas, 1962; Tighe, 1976, 1983). The purpose of this section is to present brief descriptions of the techniques, to indicate where the techniques are used, and to describe artefacts that can result from specimen preparation. Considerable patience is required to develop an appreciation of the fragility of the specimens and the skill to handle them without expensive loss.

3.5.1.1. Thin fragments, particles, and flakes

Occasionally, processed powders and small flakes of many minerals are thin enough to be examined directly. For powders and chips that are not electron transparent, additional crushing in a mortar and pestle, or between glass or ceramic plates is required (Amelinckx, 1964; Goodhew, 1972). In some layer-structure minerals such as mica, graphite, and hematite, fracture occurs parallel to easy cleavage planes and produces fragments that are thin and parallel-sided over extensive areas. Most crushed flakes, however, are slightly wedge shaped and are electron transparent only near their edges.

The crushing stresses can introduce defects such as twins, micro cracks, and dislocations, which can be imaged and accounted for in diffraction analysis. During the crushing process, it is possible to introduce contamination such as wear debris, dust, and other foreign particles.

Thin flakes can be cut from a bulk specimen with a microtome that uses glass or diamond knives. This ultramicrotomy method is useful for producing flakes from cross sections of multilayer materials such as coated metals and multiphase ceramic devices.

The bulk sample to be microtomed is encapsulated in epoxy or plastic; 20 to 80 nm slices are cut and then collected in a water bath. The cutting process produces surface striations and stress-induced damage that may interfere with the structure analysis, but should not affect the composition.

The particles and flakes are placed in an organic solvent, ultrasonically separated, and dispersed onto holey carbon films. Flakes can be stripped from a bulk sample with replicating tape (extraction replica) and redispersed onto a holey carbon film. The particles on the grid can be coated with an additional carbon film to provide an enveloping and conducting preparation. Instead of a holey carbon film, a supported collodion or other suitable organic film may be used (Zvyagin, 1967).

3.5.1.2. Thin-section preparation

Bulk samples are reduced in size by cutting slices with a slow-speed diamond-bladed saw or by grinding the sample flat with a diamond-impregnated grinding wheel. The surfaces are fine ground, polished or left in the as-received condition as required for the analysis. Typical petrographic sections are 100 to 200 μm thick. Disc-shaped specimens are cut from the petrographic thin sections with an ultrasonic drill or a diamond-core drill (Tighe, 1964).

Although discs and petrographic sections can be ground and polished as thin as 30 μm before ion thinning, experience has shown that such thin discs are extremely fragile and may not survive long enough for the complete analysis, which may require examination over long periods of time in different instruments. Extremely fragile materials and porous materials can be pressure impregnated with epoxy or bakelite before slicing and grinding. Cross-section specimens (Bach, 1970) can be stacked together and pressure mounted in epoxy or plastic before carrying out the slicing and cutting operations.

Before the element-analysis techniques were available, thin fragile specimens were cemented to copper single-hole grids. However, in X-ray microanalysis, spurious copper signals are obtained from the mounting grid and this practice is no longer recommended unless absolutely necessary. Beryllium grids are available and should be used when extra support is required.

The mechanical profiling of a disc specimen is carried out using a diamond-impregnated metal tool, a small wood dowel with diamond paste, a small metal disc or ball tool with diamond or alumina paste that is held in a variable-speed hand drill or in a semi-automated profiling machine. The specimen is cemented to a metal disc or glass slide and the processes are monitored carefully with a light microscope. When an ultrasonic tool is used it must be slightly rounded because a flat tool will produce a profile with a hump at the centre.

The mechanical profiling technique must be used with some care in order to minimize surface strain from grinding. The damage consists of cracks, embedded grinding debris, and pull-outs. It is possible for cracks to be introduced by grinding and then propagated by both the continuing contact pressure and the presence of the liquid abrasive carrier. In some cases, it may be necessary to maintain inert grinding conditions by selecting special lubricants or by chilling the sample. These mechanical profiling techniques require some practice to obtain reproducible sample conditions.

Profiling in the ion-beam thinner occurs when a well aligned beam that is smaller than the specimen diameter or less than

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2 mm in diameter is used or when the specimen edges are masked with the holder. The disc specimens can be profiled on both surfaces or one surface can be left flat. A flat surface is preferable for electron-diffraction analysis as well as for secondary electron imaging.

The mechanical preparation of specimens has been greatly simplified by the development of two instruments by Gatan Inc. (6678 Owens Drive, Pleasanton, CA 94566, USA) (Alani & Swann, 1990). The first is a holder for disc samples that is used on a polishing wheel to grind and polish discs to a specific thickness. This holder has a height adjustment for the specimen, which can be ground and polished to a thickness of 50 μm by the use of various grades of abrasive. With the second instrument, called a 'dimplerTM', the polished disc is profiled or dimpled on one side. This dimple is ground and polished with a sensitivity of 1 μm . The dimpled disc is then ready to be thinned in an ion-bombardment instrument.

3.5.1.3. Final thinning by argon-ion etching

Argon-ion bombardment or sputter etching is the simplest method for the final thinning of electron-microscope specimens. The application of the technique to ceramics and minerals was demonstrated in the early and mid-1960's with an apparatus commercialized by Paulus & Reverchon (1961; Tighe & Hyman, 1968) or similar designs (Bach, 1964; Drum, 1965). Since that time, numerous commercial instruments have been developed and are available in most electron-microscope laboratories.

The schematics in Fig. 3.5.1.1 show two types of arrangement of the instruments. There are two ion sources for etching from both sides of a specimen, a specimen holder that can be rotated, a viewing port, and a vacuum system. In the instrument in Fig. 3.5.1.1(b), the ion sources tilt instead of the specimen holder and an airlock system is used for sample exchange and for monitoring the sample during thinning. The new instruments are relatively trouble free and simple to use compared with the first-generation instruments. The ion sources operate at 4 to 10 kV with variable current to control desired thinning rate and the amount of specimen damage. Thinning rates of 1 $\mu\text{m h}^{-1}$ per ion source are average for normal specimens. The sputtering rates depend also on the angle of tilt (Fig 3.5.1.2) with respect to the ion beam. Faster rates cause more specimen heating and greater ion damage.

The Dual Ion Mill system has two chambers such as the one shown in Fig. 3.5.1.1(b) (Gatan Inc.). The chambers function independently, so that two specimens can be thinned simultaneously. The sample holder is raised through an airlock to the observation window in order to monitor the thinning process. A special beam detector can be used to stop the operation when the specimen perforates.

The specially designed Precision Ion Polishing System 'PIPSTM', provides precise control over the specimen thinning area and is a dedicated low-angle instrument with a high thinning rate (Alani & Swann, 1992). The ion beams can be adjusted individually to specific angles, and can be switched on and off regularly during the thinning process. Additionally, the beams can be oriented with respect to specific line features of the sample to preserve edge detail, for example, in a stacked sample (Alani, Harper & Swann, 1992). Gases other than argon can be used for special etching conditions.

Ionic bombardment produces uniquely etched surfaces that are easily recognized in light and electron micrographs. With stationary specimens, closely spaced grooves and ridges are etched parallel to the direction of beam impingement. When the specimen is rotated slowly, these ridges are smoothed and an

undulating orange-peel surface is produced. The severity of etching decreases when the angle of incidence to the ion beam is decreased to near grazing angles but uneven etching is never eliminated. The orange-peel texture is randomly located with

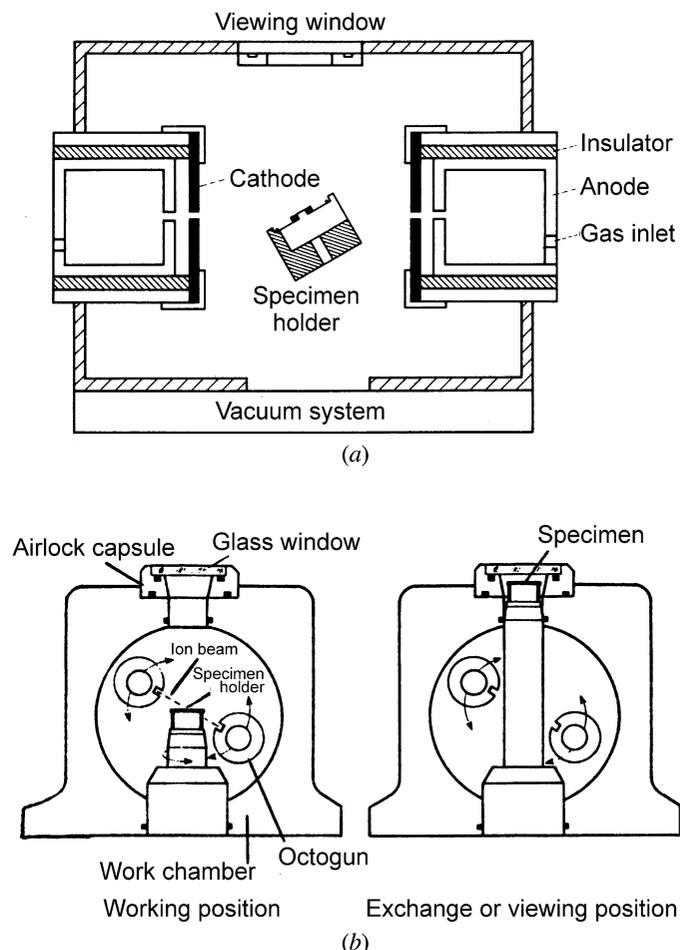


Fig. 3.5.1.1. The two types of arrangement for final thinning by argon-ion etching. (a) The system of Paulus & Reverchon (1961) with fixed ion sources, made by Alba. (b) The system of Swann with movable ion sources and an airlock for specimen viewing (drawing courtesy of Gatan, Inc.).

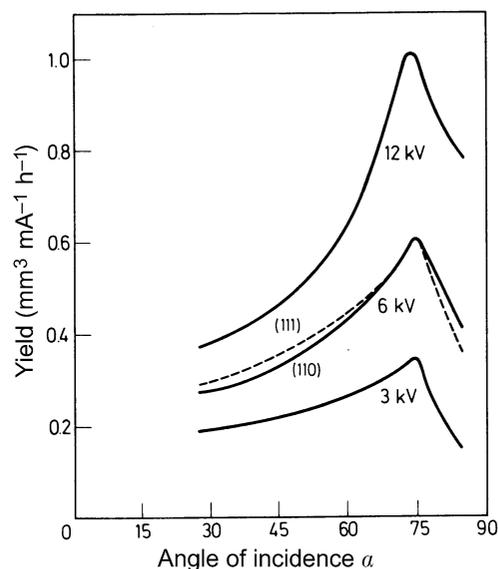


Fig. 3.5.1.2. Dependence of sputtering rate on the angle of tilt.

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Table 3.5.1.1. *Chemical etchants used for preparing thin foils from single-crystal ceramic materials; symbols: I immersion method; SFJ separatory funnel jet; CJ convection jet; BJ boiling jet*

| Material | Etchant | | References |
|--|---|--------|--------------------------------|
| Al ₂ O ₃ | 85% H ₃ PO ₄ , 723–733 K | I, BJ | Tighe (1964) |
| BaTiO ₃ | H ₂ SO ₄ | CJ | Kirkpatrick & Amelinckx (1962) |
| CaCO ₃ | C ₆ H ₈ O ₇ (dilute) | I | Braillon <i>et al.</i> (1974) |
| CoO | 85% H ₃ PO ₄ | CJ | Remaut <i>et al.</i> (1964) |
| LiNbO ₃ | KOH, 623–673 K | I | Wicks & Lewis (1968) |
| MgO | 85% H ₃ PO ₄ , 373 K | I, SFJ | Washburn <i>et al.</i> (1960) |
| MgAl ₂ O ₄ | 85% H ₃ PO ₄ , 523–723 K | I | Lewis (1966) |
| MnO | HCl + NO ₃ | | Barber & Evans (1970) |
| SiO ₂ | NH ₄ F-HF, 453–473 K | I | Tighe (unpublished) |
| | HF, 373 K | I | |
| TiO ₂ | NaOH, 823 K | I | Barber & Farabaugh (1965) |
| ZrSiO ₄ | NH ₄ F-HF + KF (1:1), 693–703 K | I | Tighe (unpublished) |
| Y ₃ Al ₅ O ₁₂ | 85% H ₃ PO ₄ , 573 K | I | Keast (1967) |

respect to grain boundaries, dislocations, and other types of interfaces found in the thin foils. The severity of the orange-peel texture increases with bombardment time.

Subsurface ion damage occurs and is imaged as spotty black-dot contrast that is typical of point-defect clusters. The presence of the ion damage affects experiments that involve heating of the thin foil but is otherwise accepted as an artefact of the process. In materials such as silicon, the ion damage is sufficient to cause vitrification of the specimen at or near the surface. The argon that is implanted in specimens can be detected with the element-analysis systems.

One troublesome artefact of the ion-thinning process is the surface contamination that is produced by sputtering from tantalum or molybdenum or stainless steel parts of the specimen holder and the cathode. Debris may interfere with the analysis. The sputter debris is frequently located along interfaces of cracks and pores and adds to the contrast effects. Additional contamination occurs during one-sided thinning. The sputter debris adheres to the non-thinning side and must be removed by light-ion etching at the end of the thinning process.

3.5.1.4. Final thinning by chemical etching

Chemical dissolution methods for preparing electron-transparent specimens were developed before ion thinning was perfected. These methods are not used extensively, but they have some advantages particularly where ion thinning may disturb the surface composition or structure of a particular material. It is advantageous to use chemical dissolution in some stages of specimen preparation, for example to relate etch pits to dislocations, to prepare a defect-free surface, and to remove the ion-damaged surface from thin disc specimens (Barber & Tighe, 1965). The thinning conditions must be chosen carefully to avoid artefacts such as preferential dissolution at grain boundaries, precipitates, and dislocations, or surface precipitates produced by a supersaturated solution.

Suitable solvents and dissolution conditions must be found for each new material. Some of the chemical etchants used for thin-section preparation are listed in Table 3.5.1.1.

Devises that squirt a jet of chemical solvent at the disc or slab specimen are used to obtain careful control over the final thinning to electron transparency (Kirkpatrick & Amelinckx, 1962; Tighe, 1964; Washburn, Groves, Kelly & Williamson, 1960).

Predictable dissolution rates are obtained by varying the concentration and temperature of the etchant. Solutions can be found that will produce a smooth surface polish or an etch-pitted surface. For example, corundum is etched in boiling phosphoric acid at a temperature approximately 50 K lower than the temperature used for polishing. Surfaces with different crystallographic orientations have different dissolution rates. Useful sources of information about possible etchants are mineralogical and chemical handbooks that discuss production of etch figures and crystallographic facets (Dana & Ford, 1922; Honess, 1927).

3.5.1.5. Evaporated and sputtered thin films

Thin nonmetallic films are prepared by electron-beam heating and by plasma sputtering for direct applications such as optical and dielectric films and for standard samples for calibration of the X-ray and electron-energy-loss element-analysis spectrometers on the electron microscopes. The thickness, crystallinity, and composition of the evaporated films are determined by the method of deposition. Co-evaporation from several electron-beam sources is used to produce films of different composition. Reproducible polycrystalline as well as amorphous microstructures are produced using heated and unheated substrates of glass, mica, metal, carbon. The crystalline electron-beam-evaporated films are used for diffraction standards and have been used to observe line broadening and lattice-spacing shifts that result from strain and compositional differences in the films.

Glasses with known compositions are used as sources for plasma sputtering to make thin-film composition standards. Such standards are required for quantitative analysis of ceramic transmission-electron-microscope specimens.

3.5.2. Metals

The aim of the specimen preparation is to obtain a sample (thin foil) of adequate electron transparency to permit the acquisition of images and diffraction patterns of the internal microstructure that is unaltered by the preparation method from that existing in the bulk material. When transmission electron microscopy is carried out at 100 to 200 keV, the sample thickness must lie in the range 0–1000 nm. The useable thickness decreases with increasing mean atomic number and with the requirement for ultra-high (atomic) resolution or for *in situ* chemical analysis by electron-energy-loss spectroscopy (Penneycook, 1981, 1982). In metallic systems, which can undergo plastic (permanent)