International Tables for Crystallography (2006). Vol. C, Section 3.5.1.2, pp. 171–172.

3.5. Preparation of specimens for electron diffraction and electron microscopy

By N. J. Tighe, J. R. Fryer, and H. M. Flower

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

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 'dimpler™', 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 μm 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 at intervals 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 'PIPS™' 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

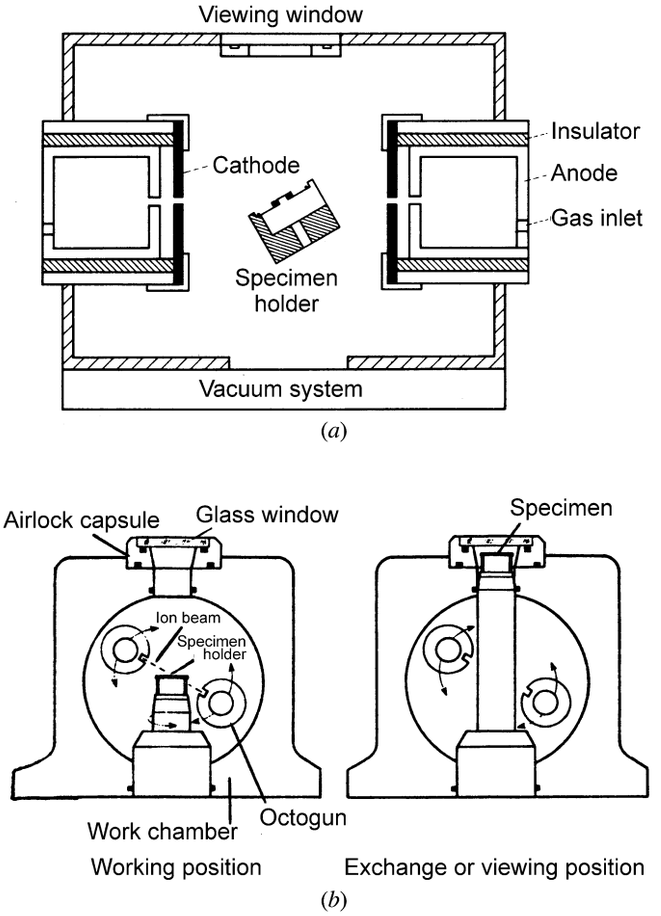

Fig. 3.5.1.1. The two types of arrangement for final thinning by argon-ion etching. (*a*) The system of Paulus & Reverchon (1961) with fixed ion sources, made by Alba. (*b*) The system of Swann with movable ion sources and an airlock for specimen viewing (drawing courtesy of Gatan, Inc.).

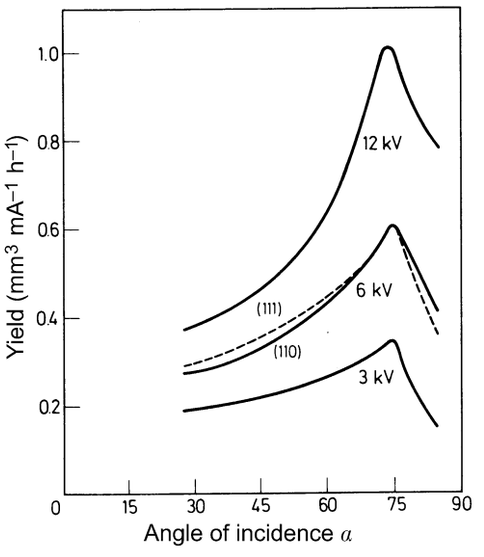

Fig. 3.5.1.2. Dependence of sputtering rate on the angle of tilt.

references