The fact that the cost of manufacturing and running a TEM tends to rise approximately linearly with accelerating voltage, combined with the high displacement damage, has led to the demise of most MeV microscopes. However there are many *medium voltage microscopes*, operating at 300 or 400 keV, which exploit the advantages of higher electron energies.

## 4.4 Scanning transmission electron microscopy (STEM)

It is possible to combine some of the advantages of the TEM and the scanning electron microscope (SEM) in the single technique called STEM. The beam is focused to as small a spot as possible and is scanned across the specimen while some signal is collected (e.g. X-rays, transmitted, secondary or backscattered electrons). This is discussed briefly in the next chapter (section 5.9.3) but the main reasons for using STEM arise from its potential as an analytical tool. We therefore leave major consideration of the technique until Chapter 7. However, many modern transmission microscopes are equipped with scanning coils which enable them to be used in a STEM mode. Such microscopes are generally called TEM/STEM microscopes in contrast to the 'dedicated STEM' instruments which are described in Chapter 7. Improvements in the electron probe size of TEM/STEM microscopes, particularly those with field emission guns, have now reduced, perhaps even eliminated, the difference in the resolution of the best of the two types of machine.

## 4.5 Preparation of specimens for TEM

It will be clear from the rest of this chapter that there are many subjects of enormous scientific and technical interest which can be studied using TEM. However, before any observations can be made, a specimen must first be prepared. It is not straightforward to make a specimen thin enough for TEM (a few tens of nanometres to a micron in thickness). The task is made harder still by the need to avoid changes in the specimen due to the preparation technique, and obtain a representative (or sometimes very specific) region. The sample must also be strong enough to handle, and last at least long enough to be examined in the microscope. These are tough requirements, and only rarely are they all met. However it is worth striving for a specimen which gives the maximum amount of information with the minimum amount of complex interpretation, and this means that a great deal of emphasis should be placed on specimen preparation. The techniques employed vary greatly, depending upon the type of material being studied, and form the subject of several books and many scientific papers (e.g. Goodhew 1985). The degree of difficulty in sample preparation can vary from being almost trivial to a skill which can take weeks to master.

The different specimen preparation techniques can be divided into two basic approaches. First is removal of unwanted material, by either chemical or mech-

anical means, until only a very thin specimen is left behind. Second is cutting, in which the sample is either cut with a knife or cleaved along crystallographic planes so that a very thin specimen, or region of a specimen, is produced. We will describe here only the basics of the most commonly used techniques.

### 4.5.1 Electropolishing and chemical polishing

The most common technique for thinning electrically conductive materials such as metals and alloys is electropolishing. The principle of the method is that the specimen is made the anode in an electrolytic cell. When a current is passed, metal is dissolved from the anode (the specimen) and deposited on the cathode. The experimental arrangement can be very simple, as shown in Figure 4.39, or can be carried out in a sophisticated semi-automatic commercial unit but the principle is identical. If the composition of the electrolyte and the operating voltage are chosen successfully a specimen in the form of a thin sheet not only becomes thinner but also smoother. Eventually a hole appears in the thin sheet and if the neighbouring regions are sufficiently smooth (i.e. well polished) they will be thin enough for viewing in the TEM. The process is shown schematically in Figure 4.40. Cooling of the electrolyte to low temperatures is often employed to change the kinetics of the etching process to produce a smooth surface. Electropolishing was the technique used to thin the specimens shown in Figures 4.15, 4.17, 4.21 and 4.24.

Automated electropolishers usually take 3 mm diameter disc samples, which emerge with a relatively thick rim supporting the thin central region. These
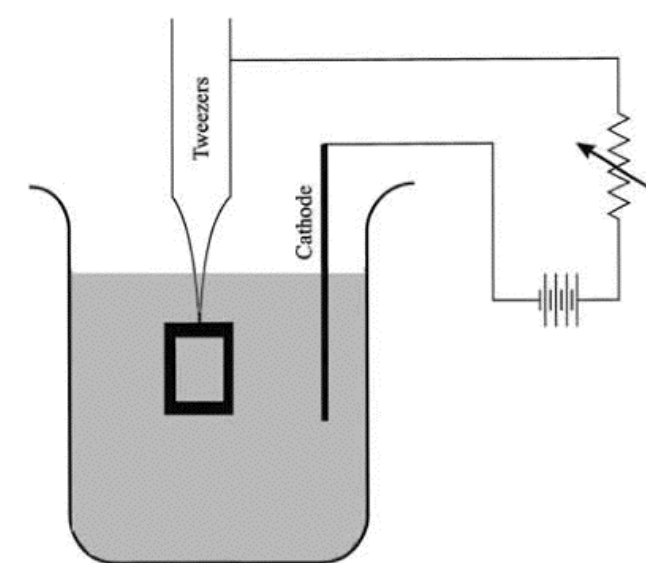


*Figure 4.39* Electropolishing as a technique for preparing thin specimens for transmission electron microscopy. At its simplest, a sheet specimen is held in tweezers in a beaker of electrolyte. A small potential (typically 1 to 30 volts) is applied between the specimen and a metal cathode.
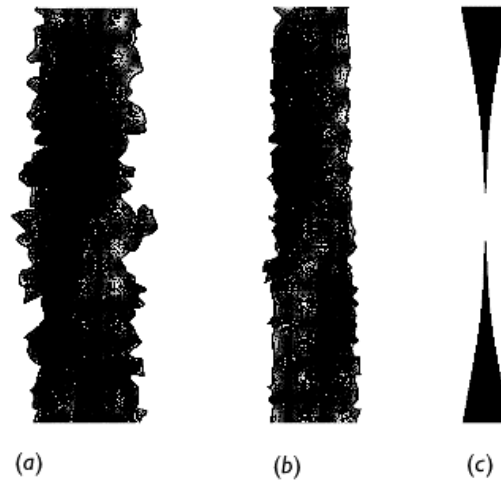
Figure 4.40 The stages of electropolishing a metal specimen. The thick, rough sheet (a) becomes smoother and thinner (b) and eventually perforates (c). The thinnest regions around the perforation should be suitable for examination in the TEM.
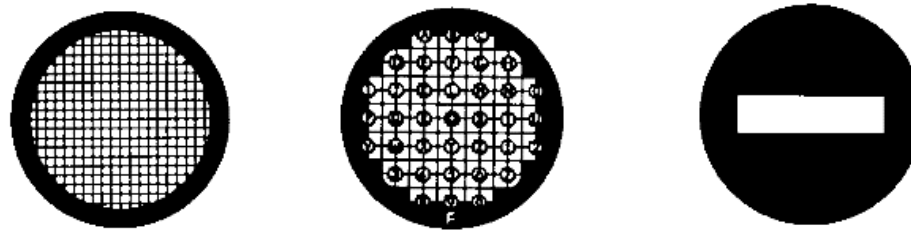


Figure 4.41 Three types of support grid for TEM specimens. From the left are shown a plain mesh grid, a 'finder' grid marked with identification letters and a slot grid for large specimens.

The stub is either immersed in the etchant or a very fine jet of etchant is directed at the centre of the specimen until a small hole appears at its centre, usually within a few minutes. The finished sample is removed from the stub by dissolving the lacquer in a solvent, and then washed in several changes of solvent to remove all traces of the lacquer. Rotation is often used to produce an even etch across the specimen. The technique is commonly employed for semiconductor specimens, using 1:5 hydrofluoric:nitric acid for silicon and Cl or Br in methanol for most III–V and II–VI type semiconductors.

When the specimen comprises more than one material, for example thin layers deposited on a substrate surface, it is often the case that one or more components of the structure are resistant to the etch used for the bulk of the material. This can be turned to advantage in the case of very thin layers which are electron transparent when the substrate is removed, but more often means that chemical etching of the substrate is followed by ion milling to produce a suitably thin specimen.

Both chemical polishing and electropolishing enjoy the great advantage that they are physically non-damaging. However, this does not mean that they do not have drawbacks, since both techniques can preferentially leach out one or more components of an alloy or compound, causing possible inaccuracies in microanalysis. Also, there seems to be no simple way to predict which etchants or electrolytes will both polish and remove material. For example, it is quite possible to be able to produce a good specimen of one crystalline orientation and a poor one of another orientation using the same etchant. Lists of tried and tested solutions are available, and new recipes are constantly being developed and exchanged.

discs fit directly into the specimen holder of the microscope (Figure 4.4(a)). Foils prepared by hand will generally need to be supported on a 3 mm grid made of copper or an alternative material which will not interfere with analysis. Figure 4.41 shows a number of types of grid.

There are many variants of the basic electropolishing technique but they share the common feature that they thin a sheet of metal from about 0·1 mm thick to perhaps 0·1 µm in a few minutes. The preparation of a foil from a thin metal sheet is therefore quite rapid, although it may have taken longer to machine or grind it to the starting thickness of 0·1 mm.

A major limitation of electropolishing is that it cannot tackle non-conducting materials. Chemical thinning, using mixtures of acids without an applied potential, is therefore frequently used for ceramics, glasses and semiconductors. There are a wide variety of techniques in use, but it is usually true that the specimen is thinned from one side only. A common technique is to mount a 3 mm disc, usually ground mechanically to a thickness of around 100 µm, onto an inert stub (often PTFE) using a lacquer which is not affected by the etchant.

### 4.5.2 Mechanical polishing

Most materials science samples will be ground and/or polished as a first stage in the specimen preparation process. Grinding is usually done using paper which has a layer of hard particles, often SiC, stuck onto one face. The paper is graded according to the particle size, which can vary from a sizeable fraction of a millimetre to only a few microns. Usually the paper is placed on a wheel which spins while being lubricated by flowing water. The specimen is mounted on a jig, often using glue or thermoplastic wax, which allows the rate of removal of material to be controlled. The sample is initially ground flat using a coarse grit, and successively finer grits are used to remove the damage inflicted on the sample by the previous stage. Final polishing is often done using diamond powder a micron or less in size, either suspended in oil or water or embedded in a plastic film. Even finer polishing can be performed using mechano-chemical means, often using colloidal silica particles floating in an alkaline liquid.

When one side has been polished, the specimen must then be turned over and the process repeated until the specimen is thin (usually just a few micrometres).

Clearly one must be careful not to thin the specimen away completely, and the final polishing stages are usually performed very carefully. Learning when to change from coarser to finer grinding or polishing steps for a given material can be a painful process; if too fine a grade of paper is used too soon much time will be spent at the grinding wheel, but if it is used too late the specimen will be useless. It is possible to thin some materials to a micron or less in thickness using special polishing pads and jigs (often using a tripod of movable control surfaces to carefully define the polishing plane). By making the specimen in the form of a low angle wedge, it is even possible to make samples which are electron transparent without the need for further treatment. However, most samples which are mechanically thinned need a final ion milling stage before they are suitable for examination (see below). The sample is usually stuck to a grid so that it can be handled using tweezers before it is removed from the jig by melting the wax or dissolving the glue.

There are several variations on this basic process. The technique is widely used for semiconductor cross-section samples, and in this case the region of interest usually lies less than a few microns from the top surface of the sample. This usually means that sacrificial material has to be glued on top of the sample to preserve the device layers. It is also common in such cases that a very specific region has to be examined, and in this case the first grind and polish step has to be performed very carefully so that the region of interest will lie in the electron transparent region of the sample. Tools have also been designed which thin the sample using a small wheel used edge-on and a grinding or polishing slurry, which gives a thick rim around the edge of the sample and added mechanical stability.

**(A)**

Dimpling

**(B)**

Grinding
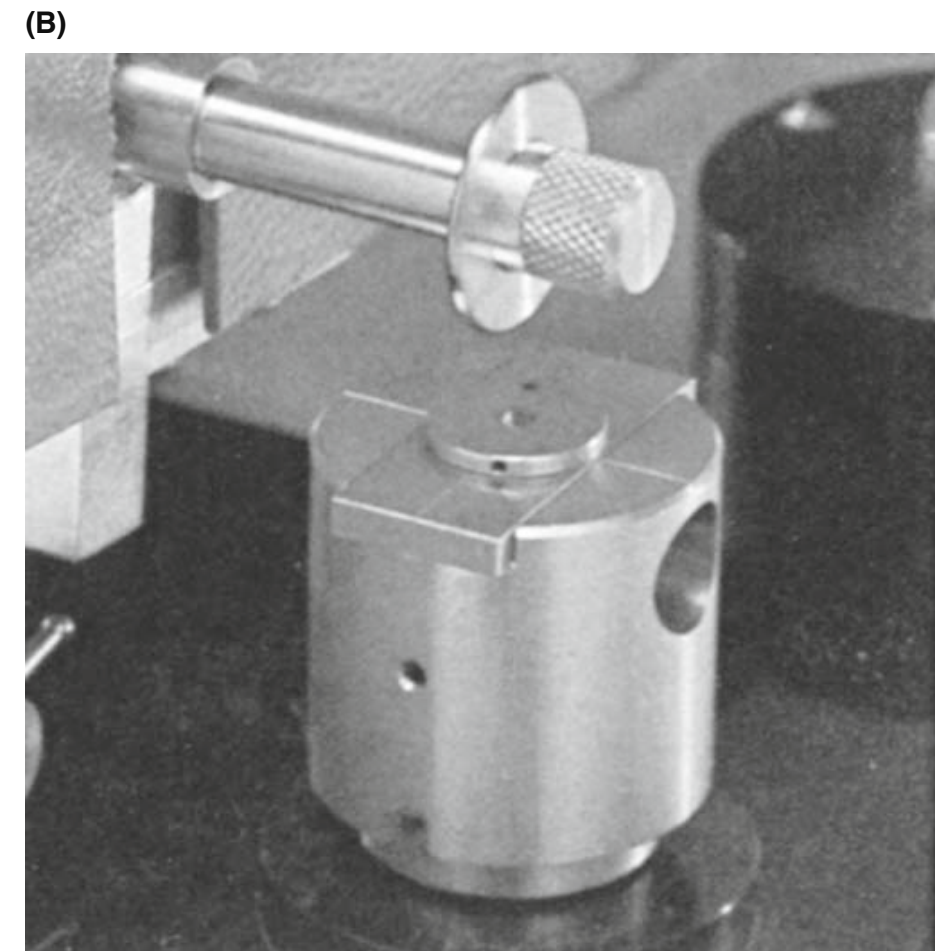
### 4.5.3 Ion and atom milling

If a beam of energetic ions or atoms is directed at a solid, atoms can be knocked out and this process, known as *sputtering*, can be used to thin specimens. A beam of ions or atoms can be generated in a vacuum using *ion* or *atom guns*. There are two types of gun which are commonly used to thin TEM specimens; those using a gas source (usually argon) and field emission ion guns, which use liquid gallium. The latter are generally restricted to focused ion beam microscopes, which are described below. There are a variety of gas source ion and atom guns, but all rely on the ability of a very high electric field (typically 1–5 kV) to generate a plasma in a low pressure gas by stripping one or more electrons from the atoms. The electric field can also be used to accelerate the ions through an aperture in the cathode, producing a beam which is directed onto the TEM sample. Two guns are usually present, so that the sample can be thinned from both sides at once. As in electropolishing, thinning usually proceeds until a small hole in the specimen is produced, which has edges sufficiently thin for TEM investigation.

The sample is usually rotated or oscillated to prevent surface roughness from developing, and if the ions make an angle of less than ten degrees to the surface it is possible to reduce problems due to different ion milling rates in specimens containing several different materials. The rate of removal varies with beam energy, incidence angle and the material being eroded, but is typically a few microns an hour. Many ion milling machines have automatic termination detectors, which switch off the ion guns when a hole appears in the sample, and liquid nitrogen cooling of the sample to reduce the effects of heating from the ion beam. Some degree of control over the ion beam can be obtained using electrostatic lenses, allowing specific areas of a specimen to be thinned.

**TABLE 10.1  Artifacts Produced During Specimen Preparation (after T. Malis)**

| Artifact/problem | Consequence |
|---|---|
| *Variable thickness* | |
| | ■ Limited local area for chemical mapping (EP, IT, C, CD) |
| | ■ Very limited area for EELS |
| | ■ Somewhat limited area for absorption-free XEDS |
| | ■ Omission of low-density defects |
| | ■ Distorted defect densities (EP, IT, TP) |
| *Uniform thickness* | |
| | ■ Limited diffraction information (UM) |
| | ■ Limited microstructure information (UM) |
| | ■ Handling difficulties (UM) |
| *Surface films* | |
| | ■ Bath residue, spec. dissolution and/or redeposition EP |
| | ■ Enhanced surface oxide (EP) |
| | ■ Extremely irregular topographies (IT) |
| | ■ Faster contamination buildup under beam (EP, R) |
| | ■ Retention of matrix on extracted particle |
| | ■ C-redeposition (UM—embedded, UM, C, R—support films) |

**Ion-beam thinning**
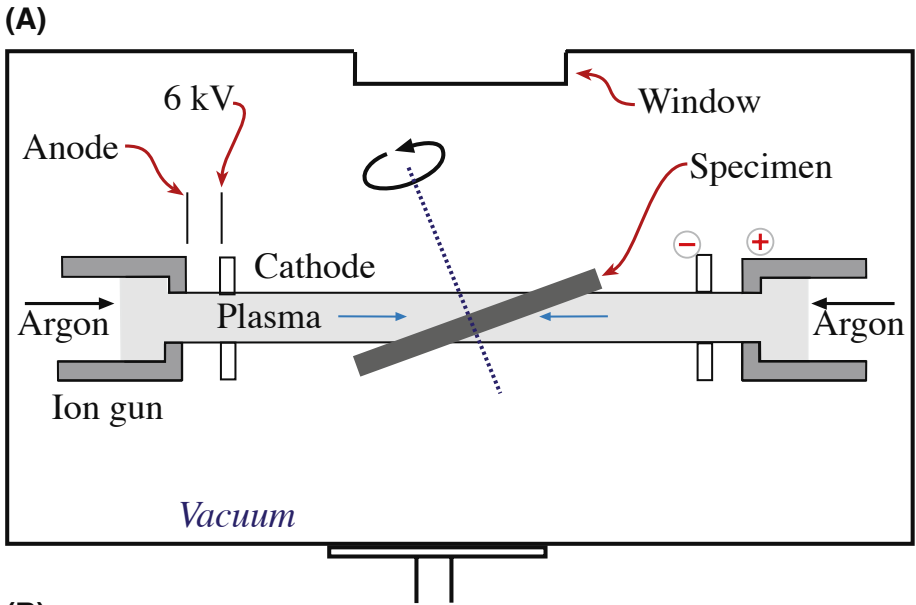
**Ion-milling**

**FIGURE 10.9.** (A) Schematic diagram of an ion-beam thinning device: Ar gas bleeds into an ionization chamber where a potential up to 6 keV creates a beam of Ar ions that impinge on a rotating specimen. Although not shown, the whole apparatus is under vacuum. The specimen may be cooled to liquid-$N_2$ temperatures and perforation is detected by the penetration of ions through the specimen. (B) Typical ion mill.
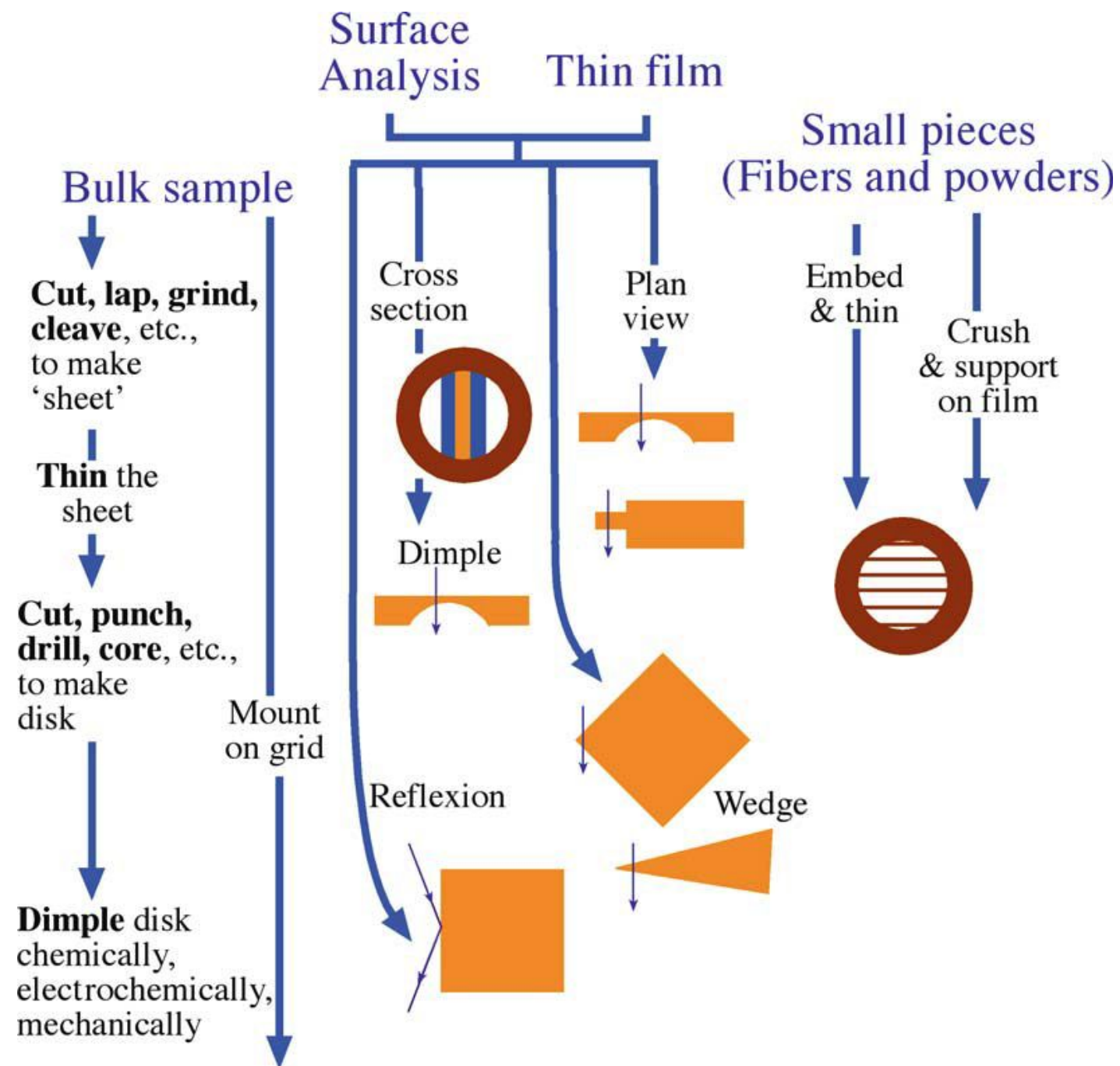
**Summary flow chart- specimen preparation**



FIGURE 10.26. Summary flow chart for specimen preparation.