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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

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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 '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 $\mu m\,h^{-1}$ 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 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

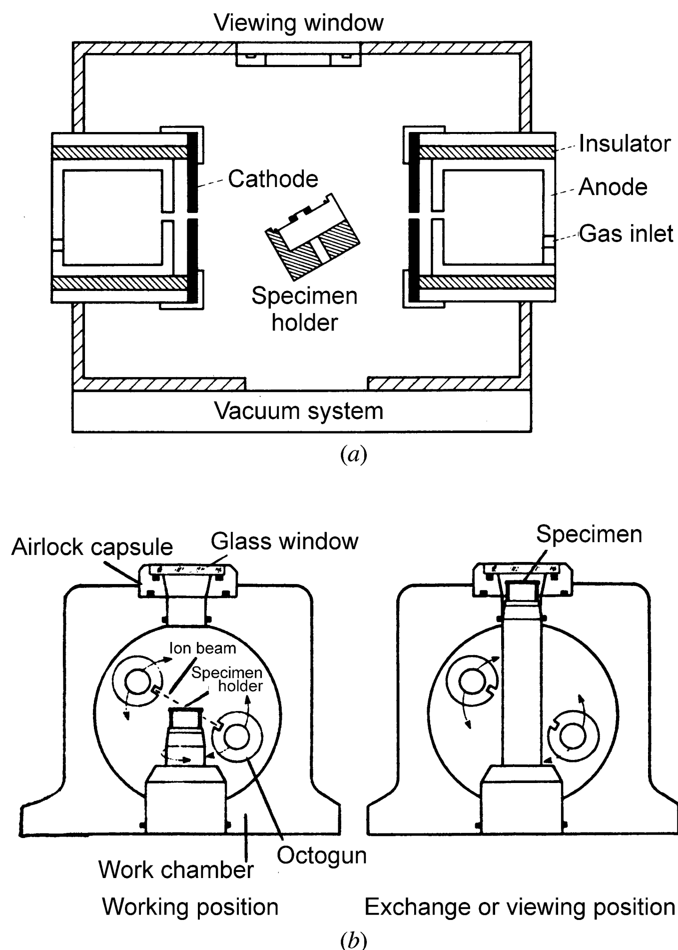

Fig. 3.5.1.1. The two types of arrangement for final thinning by argon-ion etching. (*a*) The system of Paulus & Reverchon (1961) with fixed ion sources, made by Alba. (*b*) The system of Swann with movable ion sources and an airlock for specimen viewing (drawing courtesy of Gatan, Inc.).

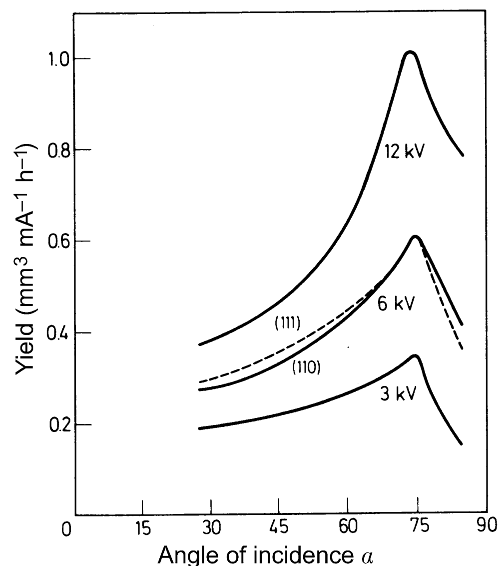

Fig. 3.5.1.2. Dependence of sputtering rate on the angle of tilt.

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_2O_3	85% H_3PO_4, 723–733 K	*I*, BJ	Tighe (1964)
$BaTiO_3$	H_2SO_4	CJ	Kirkpatrick & Amelinckx (1962)
$CaCO_3$	$C_6H_8O_7$ (dilute)	*I*	Braillon *et al.* (1974)
CoO	85% H_3PO_4	CJ	Remaut *et al.* (1964)
$LiNbO_3$	KOH, 623–673 K	*I*	Wicks & Lewis (1968)
MgO	85% H_3PO_4, 373 K	*I*, SFJ	Washburn *et al.* (1960)
$MgAl_2O_4$	85% H_3PO_4, 523–723 K	*I*	Lewis (1966)
MnO	HCl + NO_3		Barber & Evans (1970)
SiO_2	$NH_4F{\cdot}HF$, 453–473 K	*I*	Tighe (unpublished)
	HF, 373 K	*I*	
TiO_2	NaOH, 823 K	*I*	Barber & Farabaugh (1965)
$ZrSiO_4$	$NH_4F{\cdot}HF$ + KF (1:1), 693–703 K	*I*	Tighe (unpublished)
$Y_3Al_5O_{12}$	85% H_3PO_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.

Devices 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)

deformation as a consequence of the application of mechanical stress, it is most important that the stresses to which the samples are subjected during preparation are too small to result in deformation of the finished thin foil. It is also important that the chemical or electrochemical polishing employed in final thinning does not produce surface films that will either obscure the true microstructure or modify surface chemistry to the point where chemical analysis by X-ray energy-dispersive or electron-energy-loss techniques cannot be carried out. In a limited number of alloy systems, notably titanium alloys (Pennock, Flower & West, 1977), the absorption of hydrogen during preparation can also produce microstructural modifications and careful choice of electrochemical thinning conditions is required to minimize or eliminate the problem: in extreme cases, it may be necessary to resort to ion-beam thinning to reveal the true microstructure (Banerjee & Williams, 1983; see Subsection 3.5.1.3).

3.5.2.1. *Thin sections*

Samples are taken from the bulk material either by a mechanical cutting operation or by spark erosion. The former is the most common technique, but it necessarily produces a region of plastic deformation, and hence microstructural modification, in the material adjacent to the cut faces. The severity of the damage is greatest with cutting by a hacksaw or bandsaw and least with machine cutting using an oil- or water-cooled and lubricated abrasive wheel. The lubricant prevents heating of the sample, which can also lead to microstructural modification. Whatever method of mechanical cutting is adopted, it is necessary to remove a section of sufficient thickness that the slice will contain a central core of unmodified microstructure. The minimum thickness required is not only a function of the cutting method but also of the material cut since softer materials will be damaged to greater depths than hard ones. Typically, a hacksawn slice thickness will lie in the range 2–5 mm, whereas with abrasive cut-off the minimum useable slice thickness is reduced by an order of magnitude.

Subsequent thinning can be carried out by grinding using water-lubricated and -cooled silicon carbide abrasive discs to grind down from both faces of the sample to remove the regions of surface damage. As the section is reduced, successively finer grades of abrasive are required to reduce the depth of damage that they themselves introduce into the material. The depth of damage may be between 10 and 50× the depth of penetration of the abrasive particles depending on the hardness of the metal (*Metals Handbook*, 1985). Typically, grit sizes of 240 to 600 are employed to reduce the section thickness to 0.1 to 0.4 mm.

A spark-erosion method, which employs a high-voltage spark discharge between a tool and the work piece (immersed in paraffin or other insulating liquid with a high dielectric constant), can be used to perform the cutting. The metal is melted locally and eroded at the point of discharge. Both work piece and tool suffer erosion; for cutting slices, a continuously fed wire is used as the tool. With this method, cuts of the order of millimetres in depth may be made while retaining a constant tool profile. Damage at the sample surface is severe involving local melting and large thermally induced stresses. The depth of damage is typically less than 100 μm (Jansen & Zeedijk, 1972) and is readily removed from slices during subsequent thinning procedures.

From the slice, the thin foil may be prepared by either the disc or the window method. For the window technique, samples approximately 10 mm square are employed and electron-transparent sections are cut from them after the sample has been thinned chemically or electrochemically.

For the disc technique, samples of diameter to fit in the electron-microscope specimen holder (typically 3 mm) are cut from the thin sections. The discs may be cut from many materials mechanically using a suitable sample stamping machine. However, in cases where the material is either too hard to stamp successfully (*e.g.* tool steels) or so soft that unacceptable mechanical damage would result, the discs are cut out by spark machining. A tubular tool is employed and it is moved towards the sample in order to keep a constant spark gap. The edges of discs cut in this way, or by punching, require no treatment as only the central portion of the disc is subsequently thinned to electron transparency.

3.5.2.2. *Final thinning methods*

There are two main approaches to the final thinning methods: the window and disc methods (Goodhew, 1972, 1984). The window method is simple and relatively quick and produces small thin pieces of a sample that must be supported by a grid. The disc method produces a specimen where the thinned area is protected by the thick disc rim, which makes handling the foil easier. The disc method can be automated for routine specimen preparation.

In the window technique, a sample about 0.3 mm or less in thickness and ∼10 mm square is held at the edge in a pair of metal tweezers. The tweezers and the sample edges are coated in protective lacquer to form a 'window frame' about 1 mm wide. The sample is immersed in an electrolyte contained in a stainless steel beaker as a cathode. The electrolyte is stirred magnetically using a PTFE(polytetrafluorethylene)-coated stirring bar. Temperature is controlled by immersing the beaker partially in a bath of alcohol cooled with solid carbon dioxide or liquid nitrogen. The polishing rate is seldom entirely uniform and best results can be obtained by setting the specimen faces parallel to the electrolyte flow at a distance of one-quarter to one-half of the beaker radius from the centre and turning the sample through 180° periodically. Polishing is carried out until a hole appears in the sample, typically along one window-frame edge. The sample is then repositioned to induce more rapid attack on the opposing edge (*e.g.* if the hole appears at the top edge the foil must be inverted in the tweezers) and thinning is continued until a second perforation forms and grows just into contact with the first. The sample is removed from the electrolyte as rapidly as possible (it may be necessary to switch off the power to avoid the risk of sparks igniting alcohol-based solutions) and washed thoroughly in alcohol. The protective lacquer is peeled off and the sample is further washed and then dried on fresh paper towelling.

Electron-transparent regions can then be cut from the sample using a sharp scalpel. The cutting is accomplished by a pressing action rather than by drawing the scalpel across the sample as the latter can induce substantial damage. The thin foils are then mounted in the microscope specimen holder sandwiched between copper-mesh grids. The technique is particularly appropriate where very large thin areas are required and for magnetic specimens since the total mass of material introduced into the pole-piece gap in the microscope and the consequent image distortion is kept to a minimum.

In the disc technique, the sample is about 0.3 mm in thickness but takes the form of a disc of diameter equal to that of the microscope specimen holder, generally 3 mm. The disc is held in an insulating, typically PTFE, holder, which leaves a large fraction of each face of the disc exposed. The disc is connected electrically to the polishing circuit *via* a platinum wire running

down the inside of the holder and connected to a ring of platinum foil in contact with the sample disc. The sample is immersed in the electrolyte, which contains two jets through which electrolyte is pumped onto the exposed disc faces. The electrolyte flow produces more rapid dissolution at the centre of the disc than at the edges and results in the formation of a central hole. The cross-sectional profile of the thinned section is affected strongly by the size of the jet orifices and electrolyte flow rate, which requires optimization for each electrolyte/metal combination. The hole may be detected by eye using a glass container rather than a stainless steel beaker for the electrolyte with a suitable cathode immersed in it. The greatest advantage of the method, however, lies in its ready automation.

The holder and jet assembly can be mounted inside a light-tight container with a light directed onto one disc face and a photosensor onto the opposite face. *Via* suitable circuitry, the sensitivity of the detector can be adjusted to detect a hole and to cut off the polishing power supply automatically. Several such automated thinners are available commercially and provide a good means of routinely preparing thin foils.

Thin foils should always be stored in a dry dust-free environment to minimize surface reaction with the atmosphere and contamination of the thin areas. Foils of reactive metals (*e.g.* Mg or Fe alloys) will have very limited storability whereas some metals can be stored for years with no loss in foil quality either as a result of their inactivity or as a consequence of the protective nature of the thin air-formed oxide film (*e.g.* Ti).

3.5.2.3. *Chemical and electrochemical thinning solutions*

The principal requirement of the thinning solution is that material is removed from the sample surfaces in as uniform a way as possible to produce flat, polished, and clean surfaces. Thinning is carried out until perforation of the foil occurs at which time the edges of the perforated region should be sufficiently thin for electron microscopy. In a limited number of cases such thinning can be obtained chemically using a suitable acid in an aqueous or organic solvent. Comprehensive lists of chemical and electrochemical thinning solutions appropriate to a wide range of metals and alloys are given in the general references (*Metals Handbook*, 1985; Edington, 1976; Hirsch *et al.*, 1965; Thomas, 1962; Goodhew, 1972, 1975). It must be stressed that in many cases mixtures of highly oxidizing acids are employed in organic solvents and the mixing of the solutions can be hazardous unless undertaken under carefully controlled conditions involving the slow addition of acid to solvent at low temperatures. The storage of such solutions can also produce a fire and explosion hazard and all safety aspects must be thoroughly considered before preparing and using these materials. In spite of continued reference to them in texts, *under no circumstances* should solutions containing acetic anhydride be employed since they can present extreme hazards and safer alternatives exist. The use of face shields and fume-cupboard facilities are mandatory for the preparation and use of all polishing solutions and protective gloves are required in cases where strong acid solutions are employed.

Where several alternative polishing solutions are available, selection should include consideration of safety and storage aspects (inorganic acids in organic solvents being generally the least hazardous), the speed and quality of the thinning/polishing action, and the nature of the surface film that the solution produces on the finished thin foil. The surface film is particularly important where microanalytical studies are undertaken since the chemistry of the surface film may differ markedly from that of the underlying metal (Morris, Davies & Treverton 1978).

Chemical polishing solutions are very simple to use since they require only immersion of the sample in the stirred solutions at an appropriate temperature for thinning and polishing to take place. They can be employed also to thin non-electrically conducting materials such as silicon. However, the thinning action can be stopped only by removal of the sample from the acid and thorough washing of the sample surfaces. Since this operation takes a finite time, it is difficult to stop thinning in a precise manner.

Electrochemical thinning involves the application of an anodic potential to the sample and a cathodic potential to a second electrode in contact with the solution. Electropolishing occurs over a limited range of voltage and temperature and attack can be greatly diminished or halted by switching off the power supply. Thus, more precise control can be obtained over the termination of thinning and automatic control circuitry can be devised. The typical anode current/voltage (i/V) relationship at a fixed temperature under potentiostatic conditions is shown schematically in Fig. 3.5.3.1.

In region I, etching of the sample occurs. In region II, a stable polishing condition is achieved and the current density is insensitive to voltage variations. It is associated with the presence of a viscous liquid layer on the sample surface. Protuberances on the surface extend further through this layer and polish faster hence resulting in their removal and the rapid establishment of a smooth polished surface. Variation in temperature can seriously alter viscosity and the thickness of this layer and increasing temperature reduces the voltage range of the polishing plateau. Region III, which occurs at high voltages, corresponds to breakdown of the solution and gas evolution. It is necessary to establish i/V curves experimentally for any combination of metal and electrolyte. True potential–current relationships can be obtained by potentiostatic techniques (West, 1970), but in practice determination of the applied-voltage range over which polishing occurs using an anode/cathode geometry appropriate to the thinning technique to be employed is generally adequate. Since local ohmic heating of the sample can raise the temperature substantially above that of the bulk solution (Cox & Mountfield, 1967), it is necessary in either case to stir the solution in a controlled manner and to note the effect of stirring-rate variations.

At the practical level, it is pertinent to note that electropolishing to produce thin foils is very much an art rather than an exact science because of the presence of many uncontrolled or unsuspected variables in the process. Firstly, a completely fresh solution often polishes poorly because it lacks an adequate

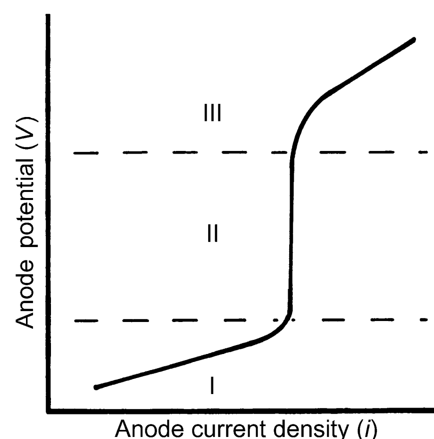

Fig. 3.5.3.1. Typical anode current/voltage relationship at fixed temperature under potentiostatic conditions.

concentration of the metal ions in solution; it is often worth adding a few drops of an exhausted solution to a fresh batch to remedy this. Secondly, solutions become exhausted, at least partially, as a result of selective evaporation, concentration of a metal-ion species, and contamination, particularly by water. Quite apart from the hazards of long-term storage, it is unwise to use solutions once these processes occur.

3.5.3. Polymers and organic specimens

The major difficulty with polymers and organic specimens is that they are rapidly degraded by the electron beam. The specimens become amorphous and sometimes volatilize (Fryer, 1987; Fryer, McConnell, Zemlin & Dorset, 1992). The rate of degradation can be reduced by encapsulating the specimen between two evaporated carbon films or by cooling the specimen to near liquid-nitrogen temperatures in the microscope (Fryer & Holland, 1984). When the specimen is encapsulated with carbon films, the structure can be preserved long enough to obtain electron-diffraction patterns. Therefore, a thin covering layer of carbon should be evaporated on top of the specimen.

Close contact of the specimen with the supporting carbon film is necessary to reduce electron-beam damage. Simple dusting of powdered specimens on carbon film is rarely satisfactory. A drop of the specimen in suspension often gives agglomerated specimens. Therefore, the powdered specimen should be dispersed in a solvent (2-propanol has proved satisfactory for aromatic compounds) with the aid of a low-power vibratory ultrasonic bath. The dispersion is then sprayed with a fine aerosol spray onto the carbon-covered grid.

For specimens where the original morphology is not important, a solution of the compound may be crystallized directly onto the carbon-covered grid. Low concentrations (1–2%) are necessary for good dispersions. Features of the crystal-growth morphology, *e.g.* spiral growth in paraffins, can be highlighted by heavy-metal shadowing. The morphology is often solvent dependent so that needles, platelets, monolayers or multilayers can be obtained as required.

3.5.3.1. *Cast films*

Thin films of polymeric compounds can be obtained by casting solutions of the polymer in a volatile, non-polar solvent onto a water surface and collecting a specimen by bringing a carbon-coated grid up though the film (Porat, Fryer, Huxham & Rubinstein, 1995). This technique is used for specimens of Langmuir–Blodgett monolayer films (Fryer, McConnell, Hann, Eyres & Gupta, 1990; Fryer *et al.*, 1991). The crystallinity of the film is often poor with this method of preparation; better crystals can be obtained by crystallizing the polymer from solution directly onto a carbon film. For many polymers, an ordered array is obtained when crystallization is performed on a cleaved alkali halide single-crystal surface. The monomer can be cast onto the crystalline substrate and polymerization performed thermally or by UV irradiation. After crystallization, the polymeric specimen is coated with carbon and floated off on a water surface. Specimens from bulk polymeric materials can be prepared also by microtome sectioning (see Subsection 3.5.1.1).

3.5.3.2. *Sublimed films*

Most organic compounds can be sublimed under vacuum to give an expitaxic layer on a suitable substrate. Specimens of compounds ranging from paraffins to polynuclear hydrocarbons (Fryer & Smith, 1982; Fryer & Ewins, 1992) and porphyrins (Fryer, 1994) have been prepared in this way. A small amount of material is placed in a molybdenum boat with a perforated cover and sublimed under high vacuum onto a heated substrate. Potassium chloride crystals cleaved in air (100) provide successful substrates. Crystal size and order increase with substrate temperature, however, and a high temperature leads to re-evaporation of the compound. Sometimes, the temperature difference between film deposition and re-evaporation is as small as 30 K. An empirical guide to the optimum substrate is one-third of the boiling-point temperature of the compound. Normally, the crystalline film produced is 10–15 nm thick and is discontinuous.

Following the compound sublimation, carbon is evaporated onto the compound and the film is floated off the KCl substrate onto a water surface. The carbon film can prevent disintegration of the organic compound. Specimens of the film are then picked up on grids.

Organic crystals easily undergo phase changes, so that the crystal modification of the evaporated epitaxic film may not be that of the bulk material. The structure may also vary between preparations on different substrates or between different temperatures on the same substrate.

3.5.3.3. *Oriented solidification*

Long-chain compounds, paraffins, phospholipids, *etc.*, can be prepared epitaxically from solution in molten naphthalene or benzoic acid (Fryer, McConnell, Dorset, Zemlin & Zeitler, 1997; Wittman & Lotz, 1990). For example, a dilute solution of a compound in naphthalene is alternatively solidified and liquified within a few degrees of the melting point to order the long-chain material relative to the naphthalene. When finally solidified, the compound is ordered along the (110) plane of the naphthalene. In practice, the final solidification is carried out on a carbon film and the naphthalene is removed under vacuum. The crystals are lath shaped and are aligned with the long-chain major axis on the carbon film across the lath and hence normal to the electron beam. Crystals of the same compounds prepared from normal organic solvents as described in Subsection 3.5.3.2 have the long-chain axis normal to the carbon-grid plane and thus parallel to the electron beam. The advantage of the normal orientation is that the large interplanar spacing along the chain axis is more accessible to direct imaging in the electron microscope.

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