

## 3. PREPARATION AND EXAMINATION OF SPECIMENS

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 hacksaw 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

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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

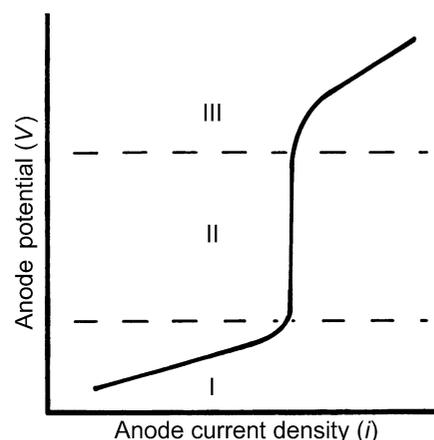


Fig. 3.5.3.1. Typical anode current/voltage relationship at fixed temperature under potentiostatic conditions.