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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

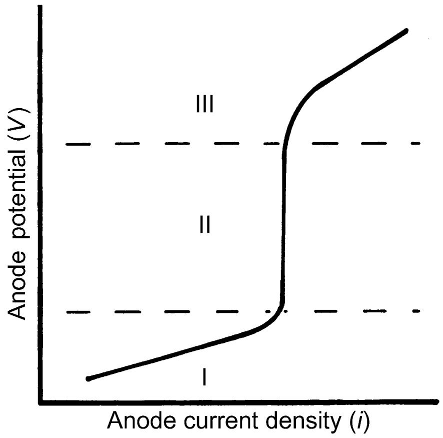

Fig. 3.5.3.1. Typical anode current/voltage relationship at fixed temperature under potentiostatic conditions.

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.

references