

# Ultramicrotomed sections in corrosion and protection electron microscope studies

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Use of the ultramicrotome to cut sections that are thin enough for examination in the transmission electron microscope has found only limited use outside biological studies. This is because the stresses involved lead to the plastic deformation of ductile materials and the fragmentation of brittle materials. Ultramicrotomy has, however, found a number of applications where conventional thinning techniques are not suitable and in the present work it has been used advantageously in corrosion and protection studies involving a number of materials: rust, high temperature oxide scales, wear debris, fretting debris, polymers, metal powders, anodic films and paints.

## 1. Introduction

The technique of mechanically cutting sections which are thin enough to be useful samples in the transmission electron microscope is a routine procedure for a wide range of biological materials. Ultramicrotomes used in the cutting of thin sections work on the principle of moving a specimen past a knife edge in repeated strokes. The specimen is advanced a small amount, the thickness of the section required, towards the knife edge between each stroke. Since biological sectioning is concerned with soft materials, knives freshly prepared from fractured glass are generally used, and only when harder materials like bone are sectioned are diamond knives found to be necessary.

Although the ultramicrotomy of non-biological materials has been most successfully applied to softer materials such as polymers and paints, a review paper by Phillips in 1967 [1] indicated that nearly all metals and alloys, ceramics and glasses can be sectioned. It was suggested that with the ductile metals and alloys sectioning occurred by shearing in a similar fashion to the action of a machine tool. The inevitable plastic deformation introduced into the sections has meant that, except in a few special cases, electrochemical thinning techniques are to be preferred. With brittle materials, like ceramics and glasses,

sectioning occurs by fracture. The unpredictability of crack propagation ahead of the cutting edge can lead to fragmentation and the production of random chips of variable thickness. Ultramicrotomy is a rapid preparation technique compared with ion-beam machining but the latter offers complete control over the thinning process and produces uniform thinned areas of known orientation.

Even with these obvious disadvantages, ultramicrotomy has found a number of applications where conventional thinning techniques are not possible, such as powders [2], thin oxide layers [3, 4], carbon fibres [5, 6], and graphite [7].

The materials of interest to the corrosion scientist are often found to be those most difficult to prepare for the electron microscope by the normal techniques of electrochemical thinning and replication. In this paper results obtained from the application of ultramicrotomy to various corrosion and protection problems are therefore discussed.

## 2. Experimental

Specimens were mounted in 00 size polyethylene pre-shaped capsules to minimize the amount of trimming prior to sectioning. The shape of the capsule used depended on the specimen form. Powders and debris where distribution was random were mounted in pyramidal tipped capsules, while

for thin films of paint or oxide, specimens were wedged at the required orientation into conical or cylindrically tipped capsules. The encapsulating resin consisted of Epon 812, DDSA and DMP-30 in the proportions 20:30:1. Residual air was removed from the encapsulated specimen by evacuation before curing at 60° C for 72 h.

An LKB Ultratome III was used to produce sections from the specimens. Before sectioning the tip of the specimen block was trimmed with a glass knife to form a truncated pyramid having an included semiangle of 60°. The area presented to the sectioning knife was as small as possible, 0.1 to 0.5 mm square, so that the risk of damage was minimized. The knives of glass and diamond had cutting angles of 45° and 50° respectively, and were set with clearance angles of 1°. Cutting speeds and section thickness depended on the particular samples but were in the range of 0.5 to 2.0 mm sec<sup>-1</sup> and 20 to 80 nm. Samples were mounted directly from the knife water bath on to 200 or 400 mesh copper grids for examination in a Philips 301 electron microscope.

### 3. Corrosion

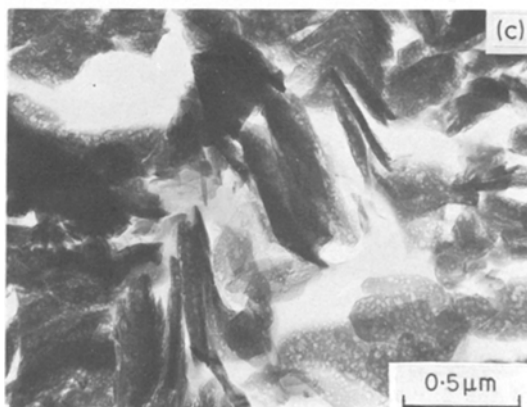
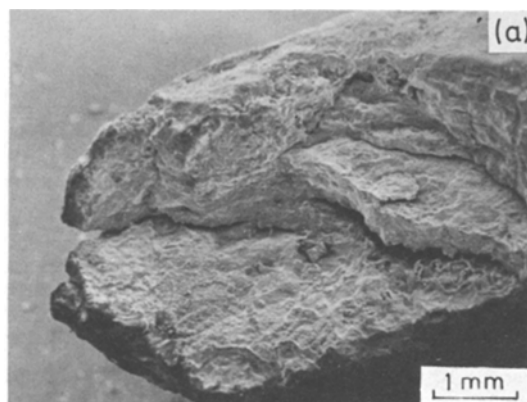
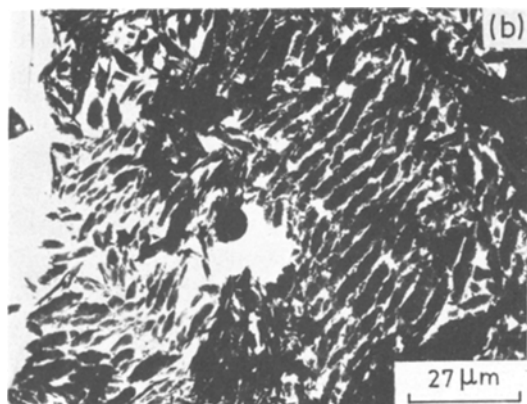
The damage caused to materials by corrosion is due to their reaction with various environments to form chemical compounds. With metals and alloys the numerous possible corrosion reactions can be divided into two general classes, wet and dry. In wet corrosion the metal is completely or partially immersed, usually in an aqueous electrolyte, and electrochemical processes occur, causing the metal to dissolve or produce insoluble or sparingly soluble corrosion products. In dry corrosion the

metal reacts directly with nonmetallic elements, usually gases, to produce a generally protective, or partially protective, film or scale on the metal.

#### 3.1. Rust

The most generally recognized form of corrosion is the rusting of mild steel. Rusting is accelerated in areas of high pollution, particularly by sulphur dioxide in conjunction with moisture and solid pollutants. Intensive examination of atmospheric corrosion has demonstrated that ferrous sulphate is present in the corrosion products of iron as discrete sites which are termed "nests". It is these "nests" of ferrous sulphate at the metal/rust interface that are the principal cause of the rapid corrosion in urban atmospheres. The initial appearance of the points of attack has been observed in scanning electron microscope studies [8] after exposures of 1 to 6 h to a humid, sulphur dioxide containing atmosphere. The results indicated that the points of attack were randomly distributed over the surface and were not confined to grain boundaries or surface imperfections. Atmospheric exposures of several months produce relatively thick layers of rust which has a characteristic

Figure 1 Thick layer of rust; (a) Scanning electron micrograph of fracture surface, (b) and (c) Transmission electron micrographs of ultramicrotomed sections.



banded structure. Sections examined in the electron probe microanalyser [9] revealed that the sites of high sulphur concentration were still active.

Although numerous mechanisms to describe rusting have been proposed, the process is still not fully understood, particularly the variable distribution of corrosion sites and their mode of growth. Surface morphological studies combined with electron probe analysis have successfully determined the reaction sites but it is now necessary to study the structural variations of the rust in greater detail.

Thick layers of rust formed over a period of years in an urban environment have an inherent banded structure which is readily visible in fractured sections, Fig. 1a. This banding of the structure is due to its intermittent growth produced by seasonal and daily variations in humidity and pollution. Microtomed sections made with a diamond knife from flakes of rust broken from the thick layer are made up of bands  $3\ \mu\text{m}$  thick, Fig. 1b. At higher magnifications, Fig. 1c, these bands are seen to have an acicular structure typical of the hydrated ferric oxide formed during laboratory experiments on thin iron foils [10].

Future studies using ultramicrotomy will include the use of X-ray analytical transmission electron microscopy to determine the distribution of sulphur in the banded structure and an attempt will be made to section the ferrous sulphate nests formed during the early stages of rusting to establish a more detailed picture of corrosion initiation.

### 3.2. Oxide films and scales

Oxidation is the result of direct reaction between metals and oxygen at high temperatures, normally in the absence of moisture and is classed as dry corrosion. The type of oxide formed controls the oxidation process and the rate at which it proceeds. Thick oxide layers or scales formed at elevated temperatures may be either protective or non-protective.

Oxidation of an alloy is complex in that the various possible metal oxides may form a solid solution, a multiphase scale may appear, or only a single element in the alloy may be selectively oxidized. The behaviour of alloys designed for use at high temperatures have been thoroughly investigated and most work is now concentrated on their improvement and in gaining a full understanding of the growth mechanisms involved. One area of

interest is the addition of rare earth elements to high temperature oxidation-resistant alloys. Work by Golightly *et al.* [11] has concentrated on the addition of small quantities of yttrium ( $\sim 1\ \text{wt}\%$ ) to an Fe-27% Cr-4% Al alloy. Without the addition the preferentially formed  $\alpha\text{-Al}_2\text{O}_3$  scale becomes convoluted, Fig. 2a, due to its lateral growth and it readily becomes detached from the metal surface on cooling. The yttrium prevents this lateral growth and assists in the formation of an oxide which adheres strongly to the surface, allowing it to withstand extensive thermal cycling.

The scales formed on the yttrium-doped alloys are relatively smooth, Fig. 2b, and oxide growth is marked by the appearance of platelets on the surface. Examination of the scale-alloy interface has revealed oxide penetration into the alloy grain boundaries, which possibly provides a 'keying' effect between the scale and alloy. However, this is not thought to be the most important effect of yttrium and it has been postulated [11] that its main role is to control the outward bulk diffusion of aluminium, so reducing the growth of the scale. Experimental evidence has shown that yttrium enrichment occurs at the sites where grain boundary penetration is occurring, but there is no evidence of yttrium in the bulk scale, which would have explained its control over the oxidation rate. The examination of thin sections of the scale is likely to provide the necessary information to verify the oxidation mechanism. Ultramicrotomed sections of stripped oxide scales made with a diamond knife were found to be difficult to prepare, and sections less than  $2\ \mu\text{m}$  thick broke up during slicing. The oxide platelets are however, readily visible on the surface of the oxide scale in sections more than  $2\ \mu\text{m}$  thick, Fig. 2c, and at higher magnifications, the faulted structure typical of oxide growth in plate form can be seen, Fig. 2d. Future work will concentrate on the preparation of thin sections of the bulk scale, and on the application of X-ray analytical transmission electron microscopy to these in an attempt to identify the yttrium distribution.

### 3.3. Wear debris

The wear damage which occurs between sliding contacts is of great importance since it controls the useful life of many mechanical components. The frictional heating occurring between the sliding surfaces and the deformation of the oxidized metal itself is sufficient to increase the

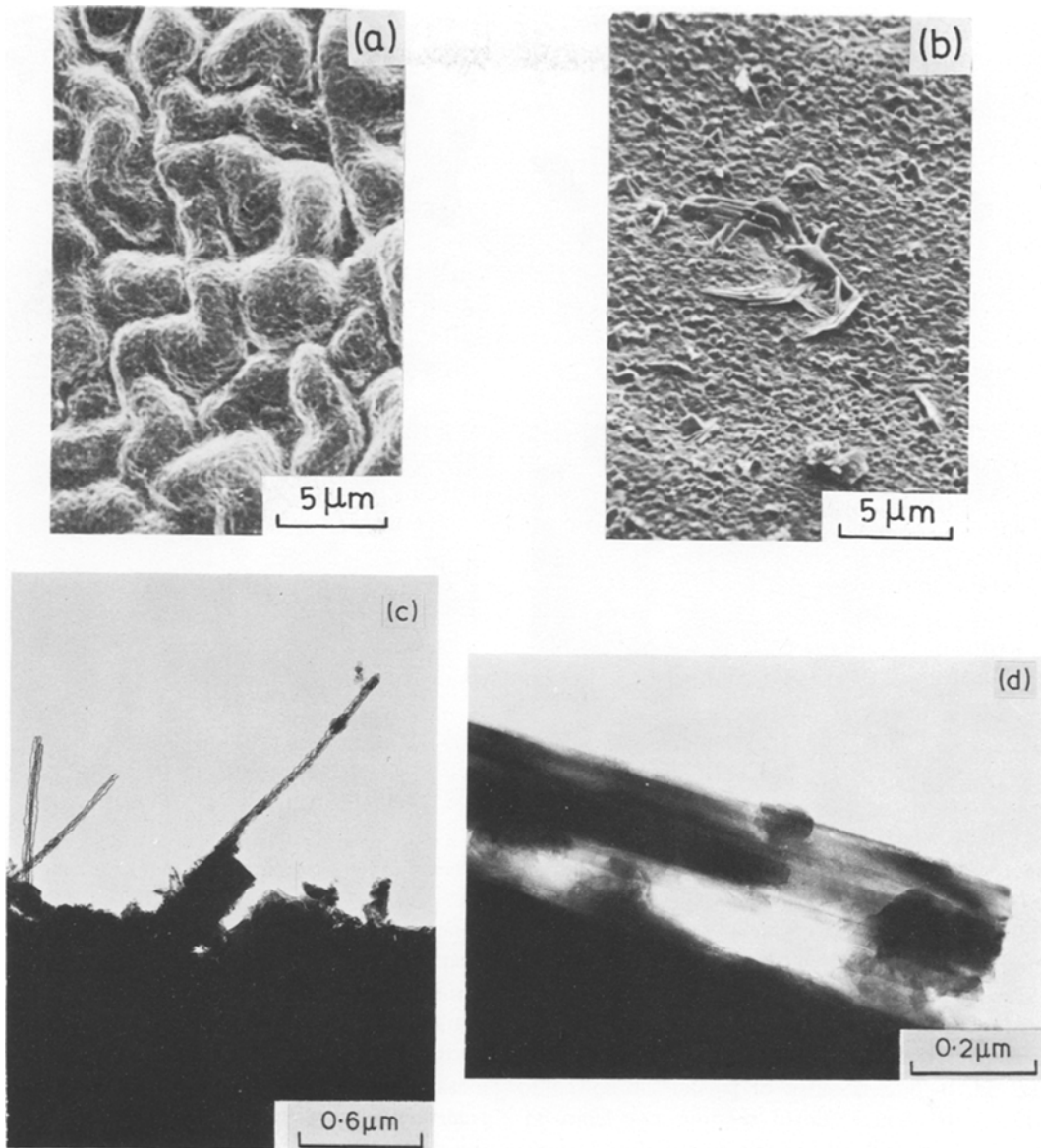


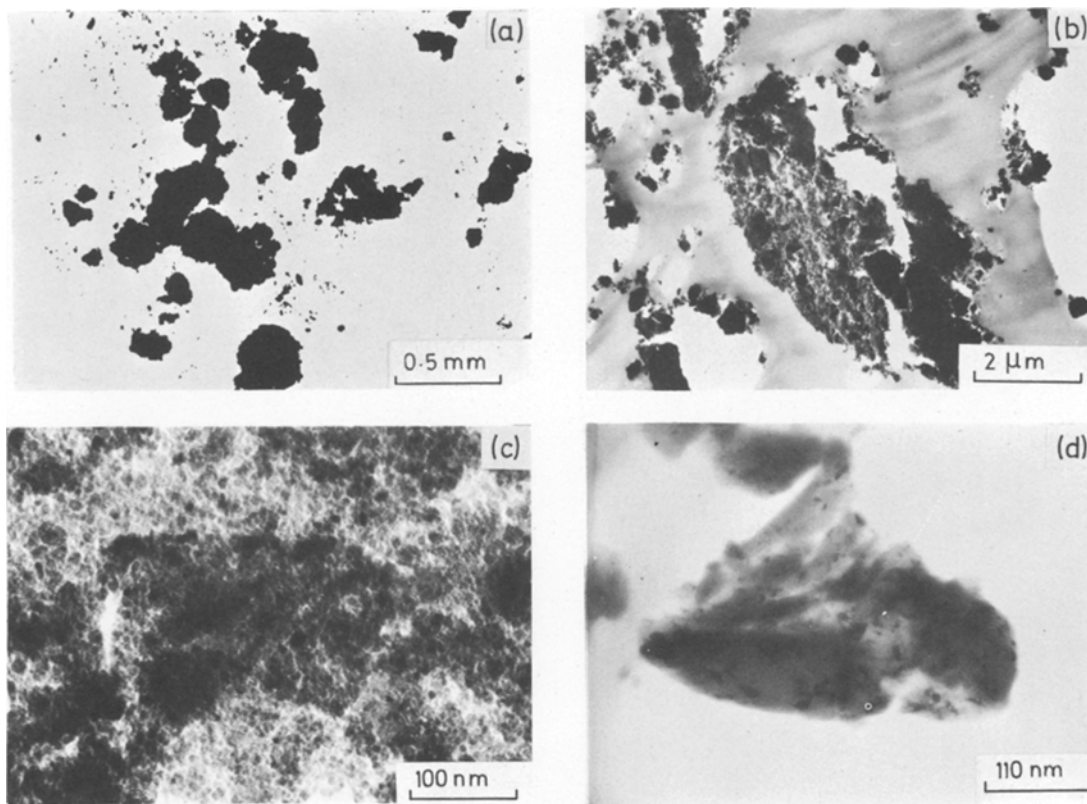
Figure 2 Surface oxide scale formed in oxygen for 24 h at 1200° C. Scanning electron micrographs of oxidised surfaces; (a) Fe-27%Cr-4% Al, (b) Fe-27%Cr-4% Al-1% yttrium, (c) and (d) Transmission electron micrographs of ultra-microtomed sections.

oxidation rate and the products of wear are wholly or partially made up of powdered oxide admixed with partially oxidized metal particles.

There has been considerable interest in recent years to classify the types of wear operative by examination of wear debris. Laboratory experiments [12] have shown that six types of wear can be identified under various sliding geometries, surface speeds and loads. Each wear type produced wear debris of characteristic morphology and

composition, which can be identified by scanning electron microscopy and X-ray diffraction analysis. The examination of debris from industrial conditions where lubricants are used has been simplified by the development of Ferrography [13]. This technique allows the wear debris to be separated from the lubricant and arranged according to size.

Since the fine oxide powder produced during wear tends to agglomerate, the debris size and



*Figure 3* Wear debris formed between surfaces of Fe-20%Cr on a pin or disc machine under a load of 86 g and at a speed of  $12.6 \text{ mm sec}^{-1}$ ; (a) Optical micrograph, (b) and (c) Transmission electron micrographs of ultramicrotomed sections through oxide agglomerates, (d) metal particle.

hence the wear type can sometimes be misinterpreted. For example the wear debris produced between the sliding surfaces of Fe-20%Cr on a pin and disc machine, appear in the optical microscope, Fig. 3a, to have a range of particle sizes, 0.5 to  $300 \mu\text{m}$ . Ultramicrotomed sections cut from encapsulated wear debris using a diamond knife, have on examination in the electron microscope, indicated that the basic particle size making up the agglomerates was 10 to 40 nm in size, Fig. 3b and c.

This sectioning technique has been found particularly useful in detecting the presence of metal particles in the bulk of the oxide debris formed in the initial stages of wear. In this example the metal particles were produced from a bulk sample with a grain size of  $30 \mu\text{m}$  and they appeared as thin sheets 0.1 to  $1.0 \mu\text{m}$  in width. The presence of oxide grains on their surfaces suggests that they were not cut from larger particles, but were separated out from the debris by the knife edge. This form of plate-like particle is similar to the

wear debris predicted by Suh [14] in the delamination theory of wear. This theory is based on the initial development of voids at dislocation pile-ups in the sub-surface beneath a layer of low dislocation density. The voids then develop by coalescence to form cracks, which grow parallel to the surface and finally lead to the detachment of the plate-like particles. The thickness of the detached plates depends on the properties of the particular metal involved and is normally in the range of 0.1 to  $2.0 \mu\text{m}$ . Although the delamination theory adequately describes the metal plates formed in the early stages of wear, the formation of the oxide debris is still somewhat obscure. It is evident from Fig. 3d that oxide grains do form on the metal surface, with a size similar to that of the basic oxide particles making up the agglomerated debris. Whether the oxide particles are made by the continued breaking-up of the metal plates until they are completely oxidized, or whether the grains are broken directly off the metal surface, remains to be answered in future work.

### 3.4. Fretting corrosion products

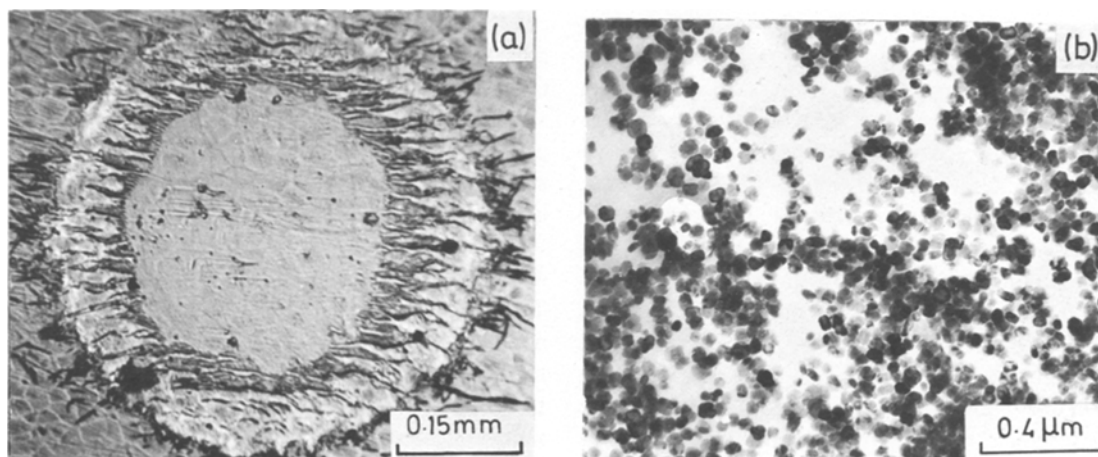
Fretting corrosion is a problem which is encountered when contacting metal surfaces are subjected to slight relative oscillatory slip. These conditions are normally produced in the presence of vibration when the surfaces are not intended to move relative to each other. The appearance of copious amounts of red debris between fretting steel surfaces and the development of scars or pits originally led to the assumption that a corrosion process was involved. Fretting corrosion is now generally recognized as a specialized form of corrosive wear and research has demonstrated that an active environment of oxygen and water vapour is essential to produce it. The methods of preventing fretting corrosion are numerous, one practised technique being to introduce polymeric material into the contact region either as an inserted layer or as a substitute for one of the surfaces. However, recent studies [15] have shown that under the right conditions fretting corrosion can be produced on metal surfaces when fretted against a wide range of industrial plastics.

Although proposed mechanisms of fretting corrosion explain the formation of the fine oxide debris, the main interest of research studies has been to determine its chemical composition and little attention has been paid to its structure and morphology. Two previously reported examinations of fretting corrosion products formed between steel [16] and aluminium [17] surfaces showed that the particles were in an agglomerated form. In the case of the aluminium oxide debris, the basic particle size was not conclusively ob-

tained, even after an elaborate sample preparation involving ultrasonic agitation.

Ultramicrotomy of embedded fretting corrosion debris allowed the identification of the basic particles during a systematic study of fretting variables; load, amplitude and frequency [15]. In the case of plastic-metal fretting couples the debris is closely associated with the plastic interface so that normal extraction replica techniques are not suitable. Higham [18] has developed a technique for extracting the fretting debris produced on flat polymer surfaces after fretting against a spherical ended steel pin using an open-tipped microtome capsule and a cold curing araldite resin.

The micro-slip responsible for causing fretting corrosion occurs in an annulus at the outside of the contact area. The fretting debris transferred to the plastic in this region has the appearance of a layer of metal, Fig. 4a. Sections through the debris indicate that it is made up of small individual platelets about 45 nm in diameter, which diffract as single crystals of  $\alpha$ - $\text{Fe}_2\text{O}_3$ , Fig. 4b. No evidence was found for the existence of free metal particles at any stage in the fretting process, which suggests that the oxide platelets are either formed by the pyrophoric reaction of small metal particles detached from the surface, or that oxide grains are formed directly on the surface, and then subsequently removed by adhesion or abrasion. Since fretting debris is retained between the fretting surfaces, it is confined to an environment of alternating stresses and elevated temperatures, and so develops a more crystalline structure than the wear



*Figure 4* Fretting debris formed between mild steel sphere and a flat nylon surface at an amplitude of  $8\ \mu\text{m}$  and a frequency of 60 Hz; (a) Optical micrograph of nylon surface. Light annular area is made up of  $\alpha$ - $\text{Fe}_2\text{O}_3$  debris. (b) Transmission electron micrograph of ultramicrotomed section through oxide debris.

debris described in Section 3.3 which is quickly ejected from the wear surfaces once formed.

### 3.5. Polymer cracks and crazes

Both thermosetting plastics and thermoplastics find use as corrosion-resistant materials, either as complete structures or as linings and coatings. Although these plastics are resistant to most agents corrosive to metals they suffer from a range of "corrosion" problems, such as solubilization, plasticization and environmental stress cracking in the presence of a wide range of organic agents. The most important of these is environmental stress cracking as it drastically reduces the strength of the plastic and its occurrence is difficult to predict with certainty.

The environmental stress cracking of glassy polymers such as polystyrene and polymethylmethacrylate is associated with plastic deformation on a microscopic scale in the formation of bands of microvoids. These bands, termed crazes, form at right angles to the principal stress and it is along these that the fracture crack travels. It has been shown recently [19] that surface flaws are readily produced in glassy polymers under a sliding spherical indenter when an active environment is present. As the stress system under the indenter is basic to many tribological processes, e.g. abrasion, erosion, polishing, scratching, wear, it is suggested that this is a possible source of flaws under practical conditions.

Since crazes and cracks have the same appearance visually, crazes were originally mistaken for cracks. The first direct observation in the transmission electron microscope [20] of the craze structure was made on ultramicrotomed sections of crazes impregnated with a sulphur-iodine eutectic. Impregnation of the crazes while being formed under stress was thought necessary to provide support for the craze structure during sectioning. Subsequent work [21], however, showed that the same craze structure could be observed in the absence of impregnation, provided microstraining was applied to the sections.

The direct sectioning of flaws formed on the surface of polystyrene after one pass of the indenter, Fig. 5a, was made on flat blocks cut from the bulk of the samples. Sections across the track parallel to the surface were made with glass knives. Although the flaws were readily recognized because of their distinct pattern no structure could be resolved in them. The defects were subjected to

microstrain and crazing occurred within them, Fig. 5b. As had been predicted from previous work the flaws which penetrated the surface to a depth of about  $60\ \mu\text{m}$  were covered by a layer of deformed polymer,  $1.0\ \mu\text{m}$  thick, so that they could not be observed on the surface.

In recent experiments when the indenter was moved back and forth once over the surface the flaws became visible on the surface, Fig. 5c and d. Sections through these showed that cracks were readily visible because although their edges were overlapping when first observed, the stress produced in the thin films by beam heating quickly opened them up, Fig. 5e. The presence of craze material was observed at the tips of the cracks and making up the secondary defects, Fig. 5f.

The lack of structure in the craze bands is due to the microvoids being closed up under the compressive stresses of section cutting so that the outline of the craze is marked only by a ripple in the surface. Since the cracks present are not healed under the compressive stresses, the technique provides a rapid means of determining the relationship of crack and craze within the flaws.

## 4. Protection

Corrosion prevention is normally obtained by proper material selection for a specific environment and, if possible, by controlling the environment, e.g. temperature, flow-rate, concentration and inhibitor additions to reduce its corrosivity to a minimum. As economics is one of the main controlling factors in corrosion engineering, the material selected is often a compromise of a relatively cheap material, i.e. mild steel which is coated with a protective surface layer. The three most common coatings are metallic, conversion (e.g. anodising) and organic (paints). Since the ability of a coating to provide protection depends on its adhesion to the substrate and its uniformity and structure, examination of the layers in section is obviously of interest.

### 4.1. Metallic coatings

The most important application of metallic coatings is in the corrosion protection of steel. The metals most commonly used are zinc, aluminium, tin and chromium, which are applied by one or more of the following processes: calorizing, mechanical cladding, electroplating, condensation of metal vapour and metal spraying. In the processes of calorizing, mechanical cladding and metal

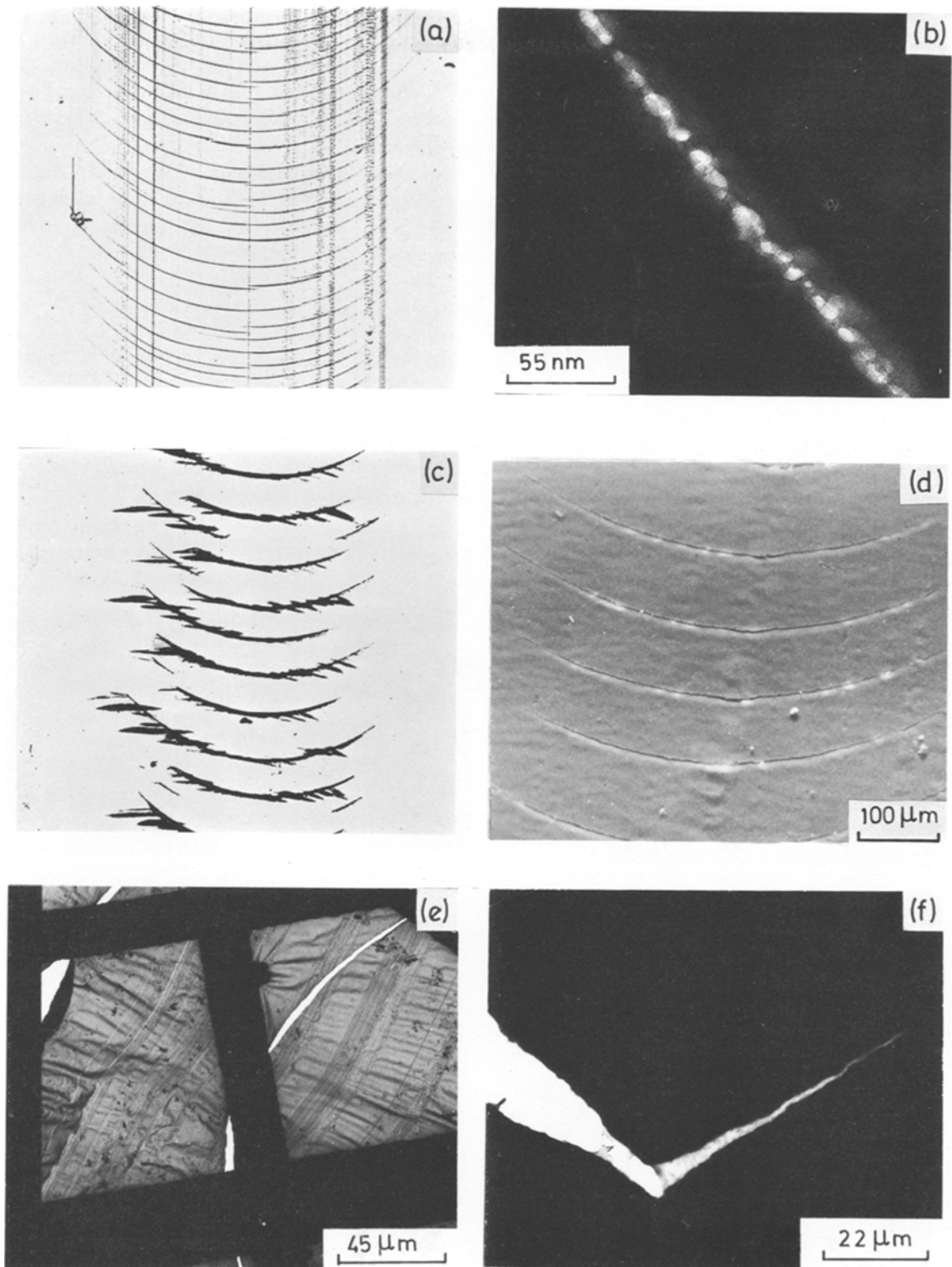


Figure 5 Flaws produced by 6.3 mm radius steel ball sliding over a polystyrene surface in air. Load 18.5 kg, sliding speed  $25 \mu\text{m sec}^{-1}$ , track width 1.2 mm. After one pass (a) Optical micrograph. (b) Transmission electron micrograph of micro-strained ultramicrotomed section. After two passes (c) Optical micrograph. (d) Scanning electron micrograph. (e) and (f) Transmission electron micrographs of unstrained ultramicrotomed sections.

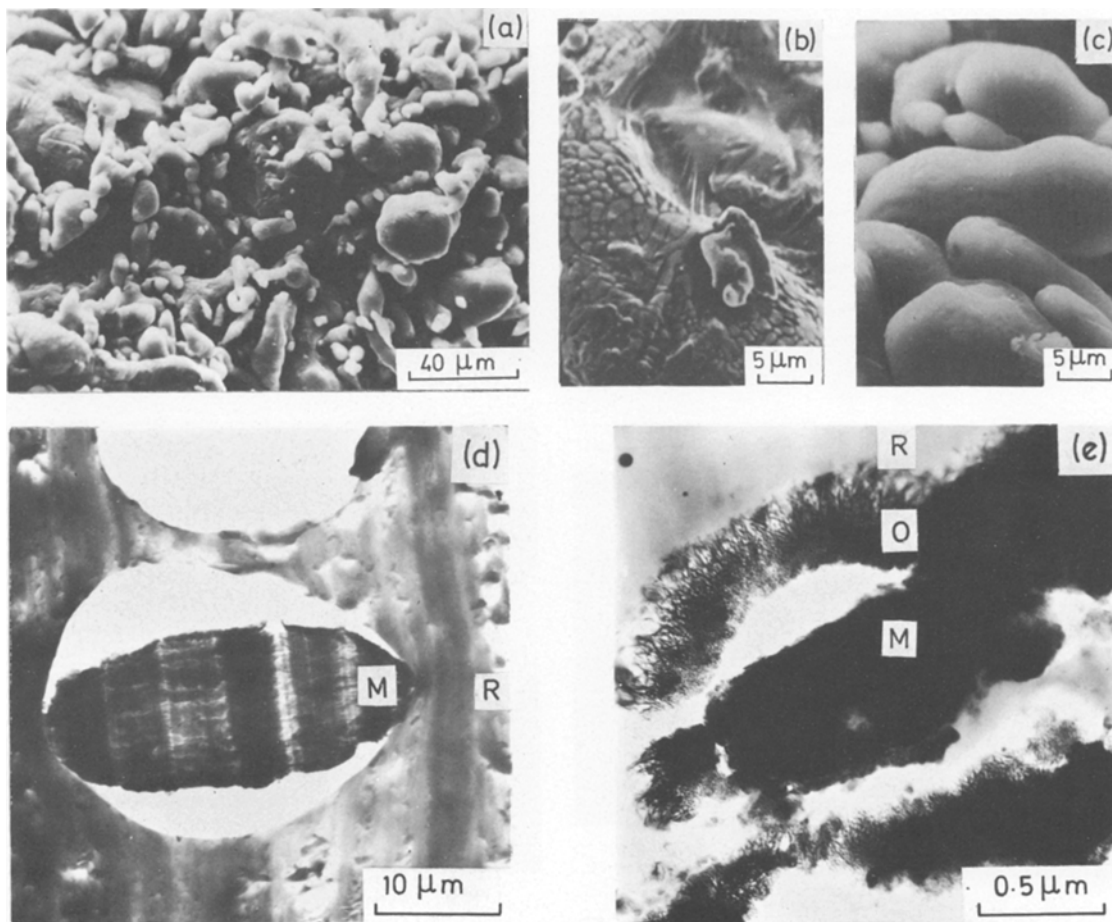


spraying the protective metal is applied in a powder form. Although these powders are of a size (100 to 5  $\mu\text{m}$ ) which is readily visible optically or in the scanning electron microscope, problems do occur in identifying the presence of surface films on the powder particles. Oxidation of the powders during their formation from the liquid, or their reaction with wetting agents, are both possible sources of contamination which could strongly influence the bonding of the final coating.

Ultramicrotomy of encapsulated aluminium powders using glass knives has been found particularly useful in assessing their quality. The as-received particles have a very irregular appearance, with surfaces that reveal grain boundaries and wrinkling, Fig. 6a and b. Powders which have been slurried in water for 5 min before drying at 120°C for 45 min and baking for 16 h at 475°C have smooth unmarked surfaces, Fig. 6c. Sections

through the particles showed that the water and subsequent treatments formed a relatively thick oxide layer on the surface which obscured the surface morphology, Fig. 6d and e. The thick banded layer (0.25  $\mu\text{m}$ ) was made up of an inner region of mottled appearance, typically 0.12  $\mu\text{m}$  thick, with an outer region of vertical needles or lamellae, typically 0.13  $\mu\text{m}$  thick. These layers provided a uniform electron diffraction pattern which agreed well with that of  $\gamma\text{-Al}_2\text{O}_3$ .

The film formed on aluminium in dry air is amorphous alumina and very thin, generally not reaching thicknesses above 10 to 20 nm even at temperatures up to 400°C. Between about 400 and 425°C and the melting point of aluminium, crystalline  $\gamma\text{-Al}_2\text{O}_3$  particles begin to form beneath the amorphous film and the metal; they are limited in thickness but spread laterally over the surface and impinge on one another [22]. A



**Figure 6** Scanning electron micrographs of aluminium powder (a) and (b) as received, (c) water treated, transmission electron micrograph of ultramicrotomed powder sections. (d) as received, (e) water treated (M = metal, O = oxide, R = resin).

featureless film 18 nm thick was observed on the as-received sample. This presumably consisted of alumina formed after atomizing the liquid metal, and there was no evidence of crystalline  $\gamma\text{-Al}_2\text{O}_3$  particles between it and the metal. The amorphous film was thicker than expected and, as it was noted that contamination was evident, the layer obviously looked thicker than it really was.

In water, orthorhombic boehmite ( $\gamma\text{-AlO(OH)}$ ) and then monoclinic bayerite ( $\beta\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ) layers develop over the thickened amorphous layer at temperatures below 60 to 80°C. Above 80°C boehmite forms alone, or more probably a complex form of this material known as pseudo-boehmite, which has a comparable but poorly crystalline structure and contains more water or hydroxyl species. These hydrated oxides often develop a needle-like morphology in their outer surface. When boehmite is heated at temperatures around 450°C, it tends to decompose into  $\gamma\text{-Al}_2\text{O}_3$  and water is removed [23]. Presumably boehmite and even bayerite were formed initially on the particles and were decomposed during baking to  $\gamma\text{-Al}_2\text{O}_3$ , retaining only the morphology of the original crystallites.

Transmission electron microscopy of ultramicrotomed powder particles of aluminium permitted the ready observation of films forced during processing. Although the metal becomes compressed in the direction of cutting the brittle layer of the oxide remained intact and retained the shape of the original particle.

#### 4.2. Anodic films

An anodic film is a surface layer formed on a metal by anodic polarization in a suitable electrolyte. The most common use of anodizing is in the protection of aluminium when a coating comprising mainly  $\text{Al}_2\text{O}_3$  is formed. The anodic oxidation of aluminium may produce one of two types of coating, depending on the forming conditions. Thin ( $< 1 \mu\text{m}$ ), compact, barrier-type films are important in the field of capacitors. The thicker porous-type films are used extensively to protect aluminium, as in the building and motor industries, to confer a decorative finish on the metal, or otherwise to change the surface characteristics to suit particular applications.

Evidence has been presented, suggesting that barrier films have a layered and/or cellular structure [3, 24]. Nevertheless, in contrast to porous films, they are relatively compact and featureless. The

porous films consist of a thin scalloped "barrier layer" next to the metal and an outer porous layer, which contains quite regular hexagonally close-packed cylindrical pores, normal to the metal surface, and open to the outer surface [25]. A carbon replica of a fracture section of such a film is shown in Fig. 7. To these two more general structure types may be added a third, which is demonstrated by the coating produced anodically on superplastic zinc-aluminium alloys in certain porous-film-forming electrolytes. This type of coating has a relatively open network structure due to the leaching out of the zinc by the anodizing electrolyte [26], the residual aluminium particles being anodized to give porous alumina films. The characteristics of these three types of coatings are sufficiently different to test the versatility of ultramicrotomy as a means of producing sections suitable for worthwhile electron microscopy.

During this work, the direction of cutting was found to be important in determining the success obtainable. When cutting so that the knife passed first through the metal, then the coating and finally through the resin (Fig. 8a), the metal and

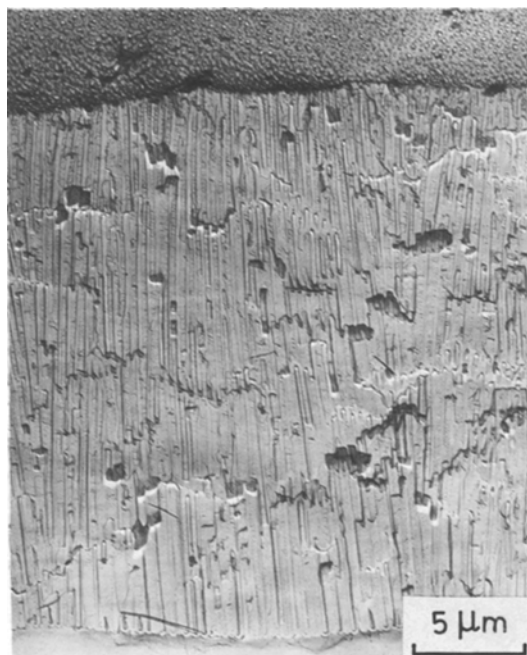


Figure 7 Carbon replica of a fracture section of a 25  $\mu\text{m}$  porous anodic film formed for 70 min at 150 V in  $0.4 \text{ mol l}^{-1}$  orthophosphoric acid at 25°C, showing the aluminium substrate, barrier layer, pores running through most of the film, and the outer surface.

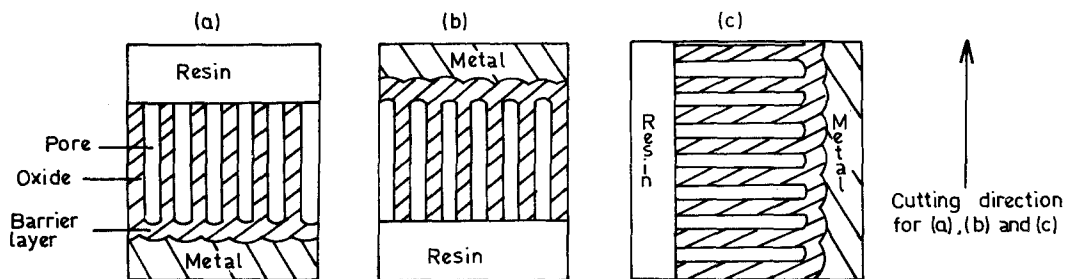


Figure 8 Schematic diagram of the face of an encapsulated specimen to be sectioned (using a porous anodic film as an example) showing the different possible orientations with respect to the cutting direction. (a) and (b) Transverse sectioning. (c) Longitudinal sectioning.

coating usually were widely separated, and the coating was left lying on the resin. This was considered unsatisfactory because it was difficult to determine which was the outer surface of the film, and because the resin tended to obscure the structure of the oxide. Similarly, the film and the substrate often became separated when cutting transversely through the coating in the opposite direction, i.e. from the resin, through the film towards the metal (Fig. 8b). However, in this case the film was often lost completely. In most instances, the most successful direction of sectioning was found to be longitudinally through the coating, such that the knife passed through metal, coating and resin simultaneously (Fig. 8c). Using this method, lengths of section showing the film

still attached to the metal were obtained, usually unobscured by displaced resin.

Certain general features are evident on most of the micrographs shown here. "Chatter" is an effect produced during slicing [2], and is seen as a periodic variation of thickness over the section. The bands run perpendicular to the direction of cutting as can be seen on the oxide of Fig. 9b. Diffraction effects appear on regions of metal section as extinction contours, which are the black areas on Fig. 9b.

Previous electrooptical studies of barrier films have been largely restricted to examinations of surfaces. However, Dorsey [3] has used ultramicrotomy to produce sections of films formed in a boric acid electrolyte. He interpreted his micro-

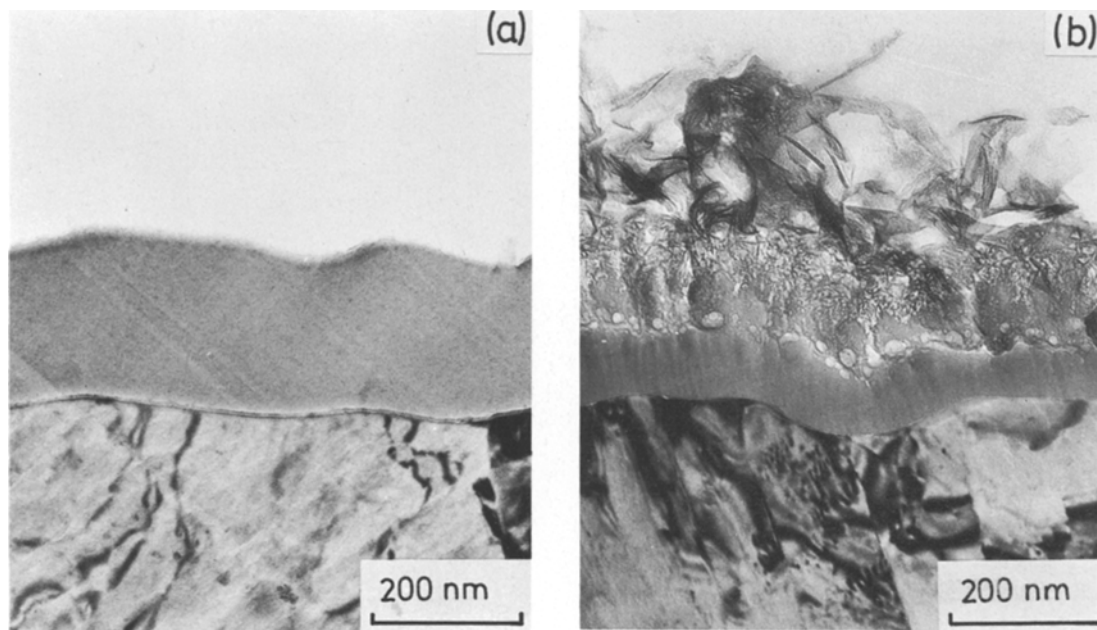


Figure 9 Ultramicrotomed section of barrier-type anodic oxide films on aluminium, formed at  $100 \text{ A m}^{-2}$  to 200 V in a 3% ammonium tartrate solution at  $20^\circ \text{ C}$ . (a) As anodized. (b) After immersion in water at  $100^\circ \text{ C}$  for 2 h.

graphs as showing duplex morphology but giving no evidence of any cellular pattern. In the present work, barrier films were formed in an ammonium tartrate solution at room temperature. Anodizing was terminated at 200 V, which would give an anticipated film thickness of 220 nm [27]. Fig. 9a is a micrograph of a section cut longitudinally through the coating showing the barrier film still attached to the metal. No duplex structuring was observed, while the apparent film thickness, 205 to 225 nm, corresponded well with the anticipated value of 220 nm [27]. The striations on the oxide layer near the metal interface were probably introduced during sectioning. The undulating metal-oxide interface is due to the pre-treatment etch, and it can be seen that the coating reproduces the contours of the metal yet remains at a uniform thickness. Because of the irregular nature of this interface, the possible existence of scalloping associated with a cellular structure cannot be rejected. However, it is anticipated that a more extensive study of barrier films using ultramicrotomy may prove very profitable in characterizing such coatings and in determining the effects of formation conditions.

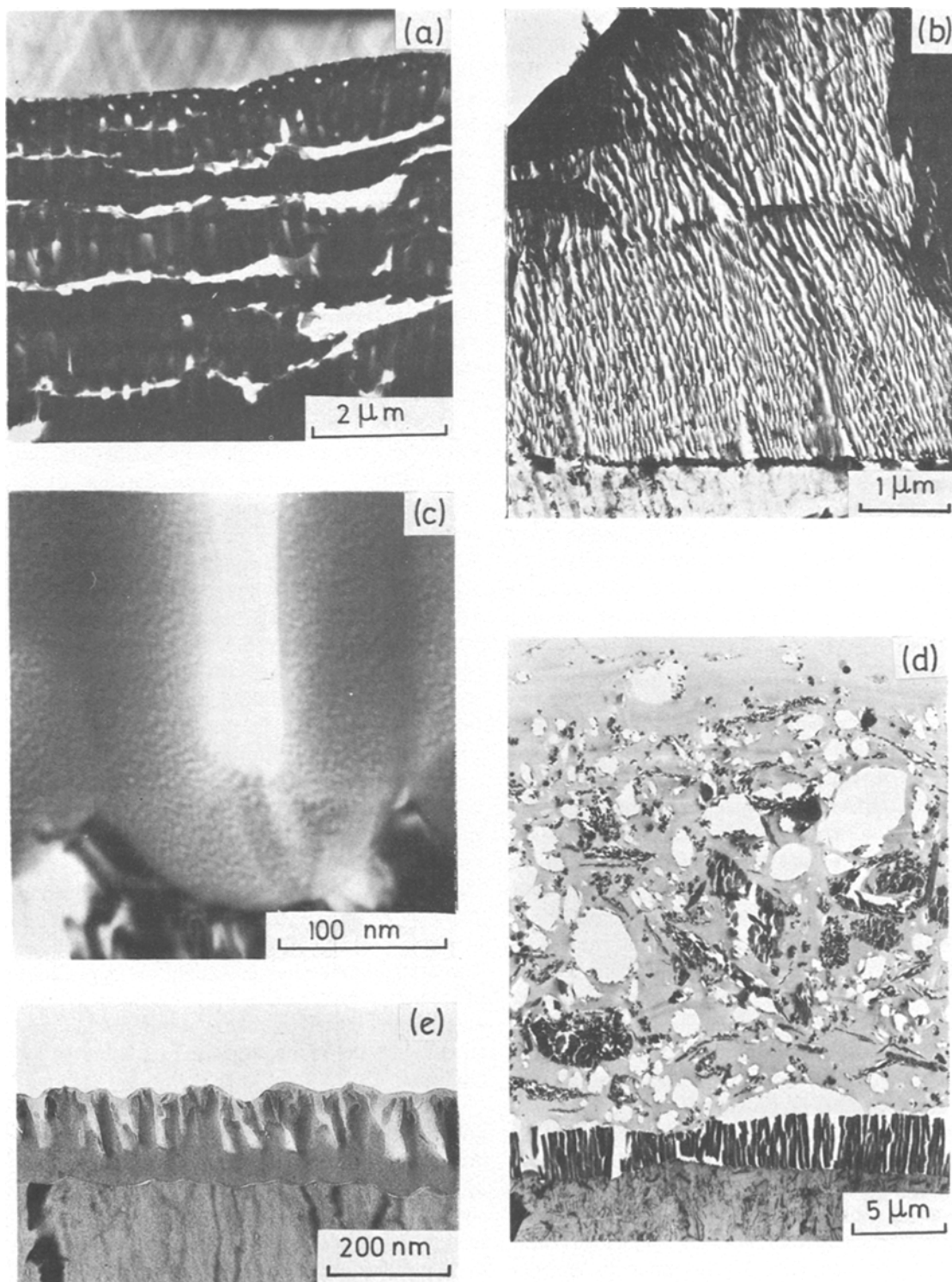
Some of the tartrate films were subjected to a 2 h immersion in boiling distilled water. A longitudinal section through such a specimen is shown in Fig. 9b, which demonstrates well the power of ultramicrotomy as a preparation technique for the examination of friable layers. Here, some unreacted barrier film is present attached to the metal, and covered by an apparently porous layer. Taken together, these two layers have about the same thickness as the original film. A striking feature in this micrograph is the friable acicular material on the surface. Previously, similar material has been observed electronoptically in plan [28] and in section using carbon replications [29]. Employing ultramicrotomy in this way, the pseudo-boehmite needles or platelets [28] may be viewed directly in section, being held at the surface by the resin. Some damage and displacement of this material has probably occurred but, nevertheless, the micrograph indicates potential lines of research where ultramicrotomy may be invaluable. These include the corrosion of aluminium in aqueous solutions, and the hydrothermal treatment ("sealing") of porous anodic films, which is an important process in the architectural anodizing industry.

Despite the excellent micrographs of sections of

porous anodic films presented by Takahashi *et al.* [4], during the present work it has been found that in general such films are rather unsuitable for successful ultramicrotomy. In most instances, the technique of replicating fracture sections [25, 30] seems to be more fruitful (e.g. Fig. 7). A typical ultramicrotomed section from a 20  $\mu\text{m}$  thick porous film, formed in phosphoric acid to 150 V, is shown in Fig. 10a. Here the cutting direction was transversely from metal to oxide, which caused the film to be detached from the substrate. The section consists of bands of porous film of varying thickness, which is probably due to the difficulty in maintaining the fracture along the same plane of pores during slicing. As the fracture jumps from one plane to another, successive cuts cause the sections to break up. A further problem with cutting transversely across the film is the difficulty in relating various pieces of fragmented section to their original positions in the coating. When cutting longitudinally through the film greater widths of continuous anodic oxide still attached to the metal substrate are obtainable. However, as shown by Fig. 10b of a 60 V oxalic acid film the disparity between the plane of sectioning and the plane of the pores creates difficulties in appreciating the morphology of the coating from the sections produced.

The main advantage of cutting longitudinally is that the coating remains attached to the metal and thus facilitates the location and consequently, the examination of the barrier layer and pore base region. Fig. 10c of an oxalic acid film formed at 75 V, shows that there is less distortion of the barrier layer than is often found in carbon replicas. This is important when measuring the dimensions of associated film features [31]. Furthermore, this micrograph reveals a more pronounced substructure in the oxide than has been achieved by replication [31].

Another benefit of applying ultramicrotomy to porous anodic films, is where pigment or hydration product have been produced in the pores by for instance, electrolytic colouring or sealing respectively. In these cases preparation via fracture sections often leads to the loss of the material in the pores before replication, or it fails to be reproduced in sufficient contrast [32, 33]. Electron micrographs of ultramicrotomed sections published elsewhere [32, 34], show pigment in the pores of electrolytically coloured films. The technique can probably be applied equally successfully



**Figure 10** Ultramicrotomed sections of porous anodic films on aluminium. (a) Formed like that of Fig. 7. (b) Formed for 20 min at 60 V in  $0.25 \text{ mol l}^{-1}$  oxalic acid at  $20^\circ \text{C}$  to give  $25 \mu\text{m}$  thickness. (c) Formed for 2 min at 75 V in  $0.25 \text{ mol l}^{-1}$  oxalic acid at  $20^\circ \text{C}$  to give  $3 \mu\text{m}$  thickness. (d) Formed like that of Fig. 9c, but coated with a layer of epoxy-based paint,  $20 \mu\text{m}$  thick. (e) Formed at  $50 \text{ A m}^{-2}$  to 50 V in  $3 \text{ mol l}^{-1}$  orthophosphoric acid at  $25^\circ \text{C}$ .

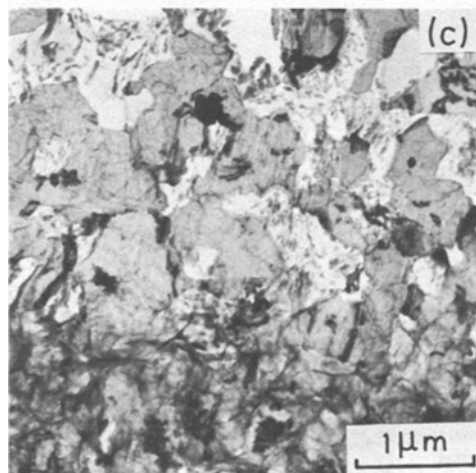
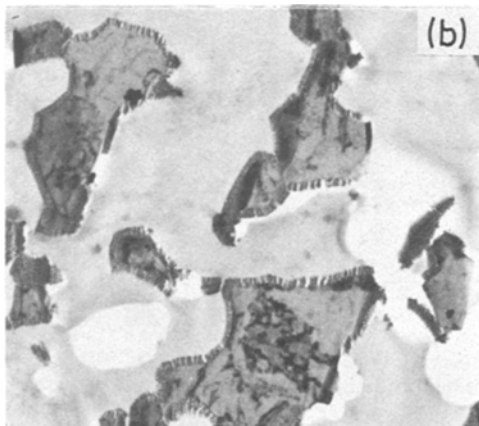
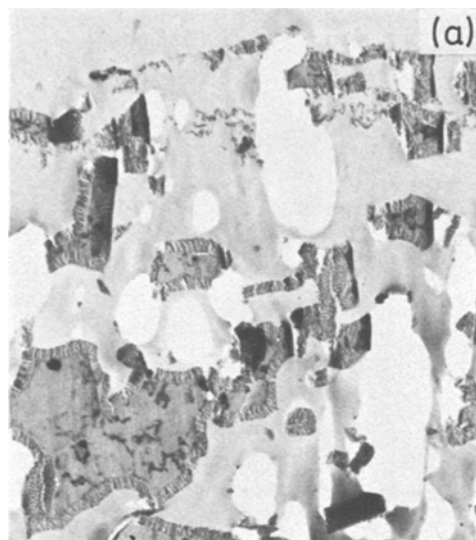
to sealed films. Also, this introduces the possibility of carrying out analyses of the pigment within the electron microscope.

For painted porous anodic films it has been found that the chemical and physical properties of paint layers cause difficulties in replication techniques [35]. As shown in Fig. 10d, ultramicrotomy enables sections of the composite to be obtained. The anodic film appears as a darker strip across the centre of the micrograph, and has suffered some lateral fragmentation due to the longitudinal cutting. The epoxy-based paint is about 20  $\mu\text{m}$  thick and merges into the encapsulating resin towards the top of the micrograph. The holes in the vehicle were probably introduced during sectioning. As the diameter of the pores in the anodic film is  $\sim 70$  nm, it can be appreciated from the micrograph that the pigment particles are probably too large to penetrate the pores. Although it was difficult to determine if the vehicle had entered the pores, ultramicrotomy may prove useful in investigating the adhesion of various coatings on to porous anodic films.

Very thin porous films, by virtue of their thinness are rather unsuitable for the fracture section technique. Fortunately, they lend themselves to ultramicrotomy. Fig. 10e is of a 50 V phosphoric acid film, about 150 nm thick, and reveals the detailed relatively undistorted structure of newly formed pores and a barrier layer about 55 nm thick, which is similar to the value predicted by  $\text{nm V}^{-1}$  ratios of 1.1 to 1.2 [25]. Thinner films may be examined even more successfully, and con-

sequently ultramicrotomy has been found to be invaluable in the examination of the early stages of film formation including the electropolishing film, and the effect of anodizing conditions on the initiation and growth of pores [36].

Fig. 11 shows portions of the section of a 85  $\mu\text{m}$  coating formed on a Zn-22% Al alloy by anodizing in phosphoric acid. Although replication techniques have been developed that allow limited study of this sort of coating [26], micrographs obtained via ultramicrotomy facilitate interpretation of both the bulk and finer structures, and permit the examination of the coating-substrate interfacial region. Figs. 11a and b show a section through the open, but continuous network of aluminium, depicting the outer surface and a central region of the coating respectively. The zinc had been dissolved by the electrolyte, and the re-



*Figure 11* Ultramicrotomed section of the 85  $\mu\text{m}$  coating produced by anodizing a Zn-22% Al alloy in  $0.25 \text{ mol l}^{-1}$  orthophosphoric acid at  $20^\circ \text{C}$  for 15 min at  $2000 \text{ A m}^{-2}$ ; (a) At the outer surface, (b) Mid-section, (c) At the interface with the unreacted alloy.

maining voids filled by resin, which was torn during sectioning, creating the holes observable in the micrographs. It can be seen that the aluminium left after zinc removal, developed a porous anodic film about  $0.1\ \mu\text{m}$  thick. Near the substrate no such porous film was observed, but small particles embedded in the resin are apparent (Fig. 11c), which may be residue of incompletely dissolved zinc grains.

### 4.3. Paint coatings

The paints of interest to the corrosion scientist are those which provide a protective coating for metals. Paints are considered temporary coatings which need re-application, the time between applications being governed by the quality of the paint and the environment to which it is exposed.

Paints consist basically of a mixture of solid particles, the pigment, suspended in a liquid, the vehicle. The vehicle dries out on application to provide a continuous film matrix in which the pigment is evenly distributed. Paints based on the traditional oil vehicle are not impervious to the passage of moisture through the dried film and are therefore not protective to metal surfaces. In order to make paints more corrosion protective the pigments and vehicle must be carefully selected with respect to the particular corrosive environment to be encountered. Primer coatings have been developed which contain chemically active pigments that inhibit corrosion of the metal surface; both red lead and zinc chromates are of this type. Another type of protection is provided by inert pigments that have a plate-like shape and form overlapping layers on drying; aluminium

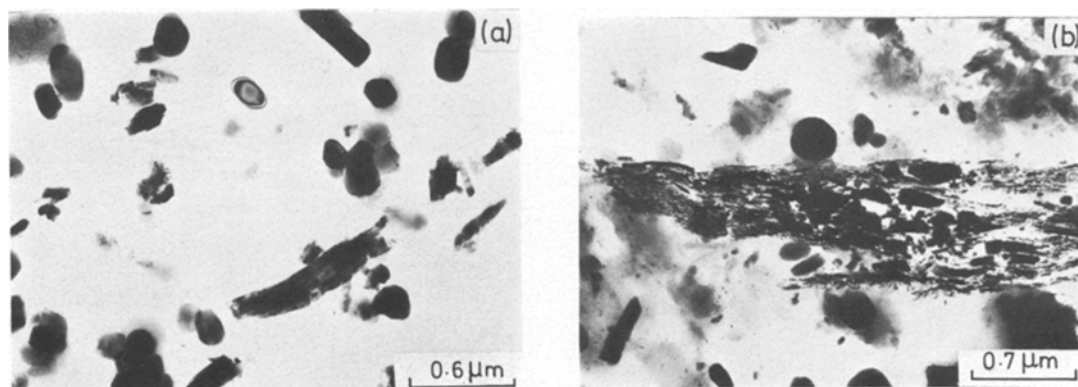
powder (leafing) and micaceous iron oxide are of this type.

Optical microscopy has for a long time been the method used to identify the pigments after they have been separated from the vehicle and re-dispersed [37]. Identification of pigments from their morphology and optical properties, in conjunction with microchemical tests, are extremely accurate but they require considerable skill and time. Examination of ultramicrotomed paint sections offers considerable advantage since, in addition to observing the size and shape of the pigments, the greater resolution allows pigment particles smaller than  $0.5\ \mu\text{m}$ , the limit of particle size analysis on the optical microscope, to be detected. Examples of paint sections are shown in Fig. 12. As the application of energy dispersive X-ray analysis in the transmission electron microscope allows analysis from areas of about  $100\ \text{nm}$  in diameter, the composition of the pigments can be rapidly determined, Fig. 13. Because the pigments are either naturally plate-like and thin, or because they have been thinly sectioned, the analysis can be quantitative without the necessity of referring to standards at the time of analysis [38].

The ultramicrotomy of paints is proving particularly useful in determining unknown paint systems involved in practical corrosion failures, the dispersion of the pigments in the matrix, and the thickness and number of paint coats involved.

### 5. Summary

In corrosion and protection studies a wide variety of different materials need to be examined in



*Figure 12* Transmission electron micrograph of ultramicrotomed sections of paint. (a) Containing pigments of titanium dioxide-circular, iron oxide-columnar and aluminium silicate-fibrous. (b) Large fibrous particle of aluminium silicate extender.

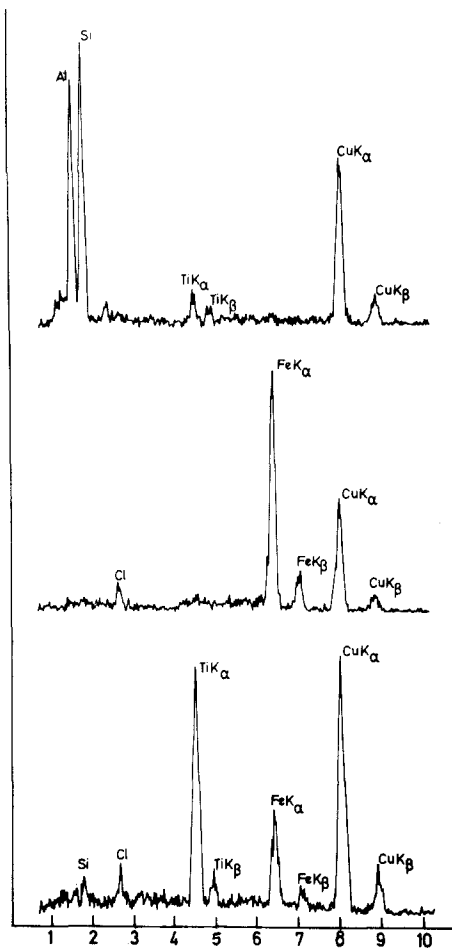


Figure 13 Energy dispersive X-ray analysis of pigments contained in the paint illustrated in Fig. 12, using EMMA-4 analytical electron microscope.

detail, which often entails the use of transmission electron microscopy. During this work consideration has been given to the suitability of ultramicrotomy to prepare thin sections of a representative selection of such materials.

The techniques most widely used for preparing specimens for the transmission electron microscope are jet electrochemical polishing for metals and alloys, and ion beam thinning for non-conducting materials such as glass and ceramics. Both these techniques require a prepared sample in the form of a disc 2 to 3 mm in diameter, with a thickness of 100  $\mu\text{m}$  or less. Where the products to be examined are of a friable nature (wet corrosion products) or are powders (wear and fretting debris) solid discs for these standard preparation techniques obviously cannot be prepared. It is possible to obtain particles thin enough for

electron transmission by simply crushing fragile materials, but this destroys any sense of orientation. Here it has been demonstrated that encapsulation and subsequent ultramicrotomy of these materials is more suitable. The embedding resin holds fragile products or powders rigidly in position, so that they may be sectioned for examination of their internal structure. This technique has been found particularly useful where only very small quantities of material are available.

Surface oxide films have been extensively examined, either by removing the films at an early stage in their formation so that they are thin enough for direct examination, or by ion beam thinning of thicker stripped films. In both cases the structural details are related to transverse sections through the film and variations in cross-section normal to the film are not revealed. Ultramicrotomy of oxide films on high-temperature Fe-Cr-Al alloys, aluminium powder and anodized aluminium has demonstrated that sections of these brittle films can be prepared, providing details of their structure and composition.

At the present time a great deal of interest is being expressed in the development of rapid techniques for examining the structure of protective surface coatings and in particular anodic films. These very hard films of aluminium oxide proved particularly challenging and this part of the work has been dealt with in greater detail. It was found that cutting longitudinally through the anodic film produced, in most cases, the best results. Useful sections were obtained from a wide range of coating thicknesses and types, ranging from the compact barrier films, less than 10 nm thick to fragile metal networks in excess of 100  $\mu\text{m}$  thickness. The hardness of the alumina destroyed the glass blades in a single cut and it was necessary to use diamond knives on sample faces that had been trimmed down to a minimum. With reasonable care diamond knives have proved to be very durable and especially in the hands of an experienced operator, enabled the relatively rapid preparation of thin sections for the transmission electron microscope.

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