(1) In general, while studying the luminescence properties of CaO phosphors care should be taken to avoid exposure to air as much as possible. Exposure to humid air especially (as in the present study) can deteriorate the quality of the phosphor drastically.

(2) The deterioration of CaO phosphor is due to its reaction with atmospheric moisture, ultimately forming $Ca(OH)_2$ which is non-luminescent. Since TL as a tool is very sensitive [4] it may be a useful a technique to study the reaction kinetics of materials where a luminescent to non-luminescent conversion takes place.

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Anisotropic electrochemical reduction of polytetrafluorethylene

New pre-treatments resulting in large increases in adhesion to polytetrafluorethylene were briefly described by Brewis *et al.* [1]. These treatments involved either electrochemically generated intermediates or the direct contact of polytetrafluorethylene with a cathodically polarized lead/antimony electrode. Since then a considerable amount of work has been carried out on the direct contact method.

The object of this communictation is to describe a novel anisotropic effect, i.e. the rate and ultimate degree of electrochemical attack is highly dependent on a skin effect in the polymer surface; this effect could be due to orientation or stress concentrations. Thus large differences are observed between polytetrafluorethylene samples of different processing histories. No similar anisotropic surface treatments have been reported for polytetrafluorethylene, although anisotropic contact angles have been observed after stretching this and other polymers [2].

The electrolyte consisted of a 0.1 M solution of tetrabutylammonium tetrafluoroborate in dimethylformamide which had been superficially dried over molecular sieves. The working electrode was a platinum wire set in glass and this was placed in contact with the polytetrafluoroethylene samples. A black carbonaceous film was formed at the point of contact which grew outwards from the electrode tip. The polarizing voltage used was ~ -2.3 V versus a saturated calomel reference electrode.

A number of polytetrafluoroethylene samples with different processing histories were examined with respect to the rate and extent of electrochemical etching. These materials included pressed sheet (Fig. 1), skived tape, unsintered calendered film and ram extruded rod (Fig.2). In ram extrusion surface layers of the polytetrafluoroethylene are subjected to large shearing forces and much alignment of polymer chains is expected; this has been confirmed by means of birefringence studies. The electrochemical attack of this material was also highly anisotropic (Fig. 2). The unsintered calendered film which also received severe unidirectional processing has been shown, by attenuated total reflectance infra-red analysis, to have a high degree of orientation [3]. When this film was subjected to the electrochemical pre-treatment it showed even more marked anisotropy than the extruded rod. As expected, for pressed sheet, no preferential attack occurred while for skived tape, some orientation induced by the skiving process is probably responsible for the slight anisotropy.

Figure 1 Photograph of electrochemically reduced pressed PTFE sheet, × 7.5.

Figure 2 Photograph of electrochemically reduced ram-extruded PTFE rod, × 2.5.

The importance of the skin effect was confirmed by treating a piece of ram-extruded rod with sodium/naphthalene/tetrahydrofuran and then removing the black layer with fuming nitric acid followed by concentrated sulphuric acid. When this process was repeated until about 3 μm of the polymer surface had been removed, subsequent electrochemical etching was isotropic.

A quantitative estimate of the rate of anisotropic attack has been obtained using the technique of chronoamperometry adapted from the study of oxide formation on metals [4]. Hence for two-dimensional surface growth of a carbonaceous film, the initial slope of the corresponding current/time curve is directly proportional to the rate of electrochemical attack. Table I shows the sensitivity of this technique to the presence of a skin effect.

The exact reason for anisotropic attack is uncertain. It is known that the reduction proceeds via conducting carbon [6] and should, therfore, be facilitated by the alignment of polymer chains. However, stress concentrations in the samples may also be important. Such stresses are probably the

TABLE I Examination of the skin effect with ram extruded rod using chronoamperometry

Diameter (mm)	Thickness of surface layer removed prior to electrochemical treatment* (μm)	Applied potential† (V)	Average initial slope of $i-t$ transient (μA sec^{-1})	Standard deviation
4	0	− 1.6	70	7.5
	3.6	− 1.6	7.5	1.4
	4.1	− 1.6	4.0	1.2
10	0	− 1.6	34	8.7
	1	− 1.6	14.5	2.9

*A layer of stated thickness of PTFE was removed chemically as described in the text.

†Versus the cadmium amalgam reference electrode [5].

cause of cracks which form perpendicular to the direction of maximum growth on etched extruded rod. The preferential reduction of stressed polytetrafluoroethylene thus presents a situation analogous to the preferential oxidation of stressed metals in which the cause is considered to be a lowering of the oxidation potential [7]. Further work on anisotropic reduction and related subjects is in progress and will be published in due course.

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Depth-resolved ^{57}Fe conversion electron Mössbauer spectroscopic studies of iron implanted aluminium

Recently, a number of ^{57}Fe conversion electron Mössbauer spectroscopic* (CEMS) studies of ^{57}Fe ion-implanted solids have been made in which the total flux of back-scattered conversion and Auger electrons were recorded by use of an He/CH_4 flow detector. In this way, depth-integrated CEM spectra of the outermost hundred nanometres or so of the implanted foils were obtained and information relating to the number and nature of the ^{57}Fe ion-implant-sites gleaned [2–6]. A natural extension of this work is to obtain depth-resolved CEM spectra using a β-ray spectrometer [7–10]. In such an experiment, ^{57}Fe Mössbauer spectra are recorded at various spectrometer settings (corresponding to various electron energies) near and below the full iron *K*-conversion electron energy of 7.3 keV. Depth resolution is, therefore, achieved because Mössbauer spectra recorded with electrons near to the full energy reflect regions close to the surface whilst those recorded with lower energies regions deeper within the sample as these latter electrons are more likely to have suffered inelastic collisions before leaving the surface. As an indication of the probing depth we cite the example of a thick aluminium sample uniformly doped with a low concentration of iron ($\sim$ 1%) throughout its thickness. From the calculations of Krakowski and Miller [11] it can be estimated that electrons with final energies of 6.5, 7.0, 7.2 and $>$7.2 keV most probably arise from depths of $\sim$ 1200, 600, 300 and $<$ 300 Å within the sample, respectively. Clearly as these depths are of similar magnitude to those commonly employed in ion-implantation experiments, it is to be expected that the method will have useful applications in this area and we make here a preliminary report of a study of ^{57}Fe implanted aluminium foils.

A 2 cm^2 aluminium foil of thickness 0.125 mm was implanted with 1×10^{17} ^{57}Fe implanted atoms cm^{-2} by a 85 keV ^{57}Fe$^+$ beam using the ion-implantation facility at AERE, Harwell. Under these implantation conditions the initial implant profile is Gaussian and the penetration depth is calculated to be $\sim$ 600 Å with a width of 240 Å at half-peak height. It is, however, to be expected that because of subsequent sputtering of the surface, the initial peak will move towards the

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*For a recent review of this technique see [1].