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 (~ 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 ~ 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 ~ 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].

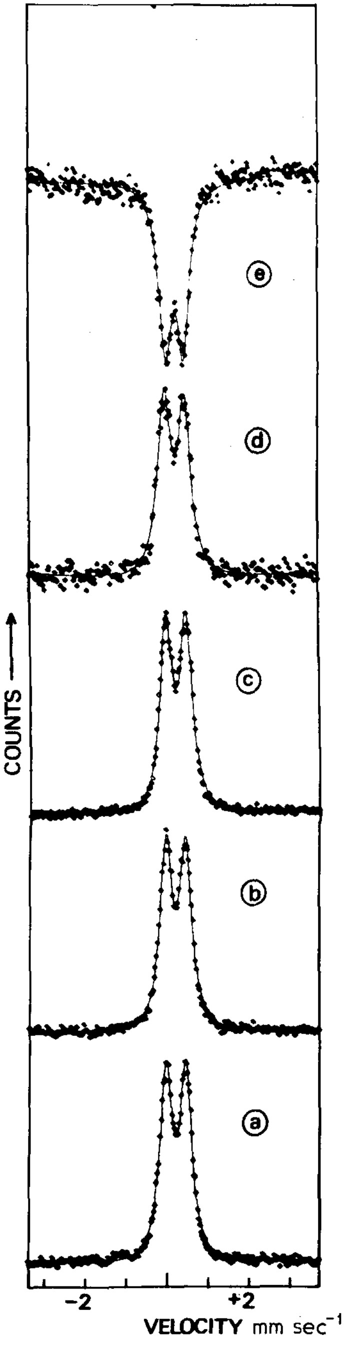

Figure 1 CEM spectra from ^{57}Fe-implanted aluminium foil using a 30 mCi ^{57}Co/Rh source. Collection times were ~ 24 h and the percentage effects for the energy analysed spectra close to 400%. (a) Total flux spectra; (b) $I = 0.56$ Å; (c) $I = 0.60$ Å; (d) $I = 0.64$ Å; (e) Room temperature transmission spectrum.

surface (by the amount sputtered) and that the implant profile will be flat from this depth to ~ 600 Å. It is also expected that the total concentration of ^{57}Fe will not be significantly changed as a result of sputtering. Fig. 1 shows CEM spectra of the foil recorded at various spectrometer settings* (see Fig. 2) together with a conventional transmission spectrum. The CEM spectra consist of two resolved peaks whose line positions are similar to those observed by Sawicki *et al.* [2, 3] for aluminium foils implanted under similar conditions. Sawicki *et al.* assigned such spectra to a quadruple doublet arising from iron atoms associated with another iron nearest neighbour. If this assignment is correct, such dimers are the predominant species within the foil. The spectra were computer fitted to two Lorentzians on the assumptions that they consisted of quadrupole doublets. Acceptable fits were obtained and the derived parameters are given in Table I. It can be seen that, although the isomer shift remains constant within the experimental error, there is a small but significant increase in the quadrupole splitting as the spectrometer setting increases; i.e. as the energy of the detected electrons increases. The origin of this effect is still under investigation but it may arise from either one or both of the following. Firstly, for high-dose rates, it is to be expected that considerable radiation damage will occur in the outermost surface regions of the foil which could lead to an increase in the asymmetry of the environment of the iron atoms close to the surface. Some support for this view comes from the recent work of Jain and Longworth who have observed anomalies in the CEM spectra of copper foils implanted with high doses of ^{57}Fe [5, 6]. Secondly, it is not unreasonable to suppose that the increase in quadrupole splitting arises from an increase in the asymmetry of the iron environment as the surface is approached due to the presence of the surface itself. In this context Minkova *et al* [12] have also observed anomalously large quadrupole interactions attributed to surface effects in γ-FeOOH, but these data related to thin films (tens of Angstroms

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*It should be noted that these settings are not readily related to depths because of the non-uniform distribution of Fe atoms within the foil.

thick) rather than the surface regions of a thick sample.

The Mössbauer parameters ($\delta = 0.151$ $\Delta = 0.438\,\mathrm{mm\,sec^{-1}}$) of the transmission spectrum (Fig. 2) are rather different from the back-scattered spectra, and it is likely that this spectrum arises from impurity iron atoms distributed throughout the bulk of the specimen. This view is confirmed by the observation that no magnetic hyperfine splitting was observed by us in a transmission Mössbauer spectrum recorder at 77 K, whereas, Sawicki *et al.* [2, 3] have detected magnetic ordering, in the surface regions of aluminium foils with similar implant concentrations, by total flux CEMS measurements.

It should be noted that this type of direct fitting of the back-scattered electron Mössbauer described above is only an approximate procedure. Baverstam *et al.* [7] have pointed out that the spectra recorded at various spectrometer settings are in reality linear combinations of spectra arising from all depths within the samples. For a particular setting (E) the number of counts recorded in the nth channel of the Mössbauer spectrum is

$$T(E)_n = \int_0^\infty w(E,x)P(x)_n dx$$

where $P(x)_n$ is the emission probability of electrons at depth x and $w(E,x)$ is a function which gives the probability for an electron released at depth x has of being recorded at a spectrometer setting E. For spectra recorded at various energy settings (E_j) a set of (overdetermined) equations may be written which express each recorded spectrum as a linear combination of sub-spectra arising from ith layer of thickness 1, namely:

$$T(E_j)_n = \sum_{i=1}^{I} \left[\int_{1_i}^{1_i+1} w(E_j,x)\mathrm{d}x\right] P_{in}$$

$$j = 1, 2, \ldots, J.$$

In this expression J is the number of spectra measured, I is the total number of layers and P_{in} unknown coefficients. In order to extract the unknown coefficients P_{in}, and hence the Mössbauer spectra of the ith layer, the form of the weighting function $w(E, x)$ must be known. We are currently determining this function for our spectrometer by the recent method of Bonchev *et al.* [13] but inspection of the calculated weight functions of Krakowski and Miller [11] indicate that a detailed analysis of the data in Fig. 1 would tend to exaggerate the difference in quadrupole splitting between those iron atoms located close to the surface and those located deeper within the foil. From the above it is also clear that for samples where the function $P(x)_n$ is a function of depth concentration of the Fe implants alone, that this depth (x) dependence of the concentration may be readily extracted from the background corrected electron spectrum (Fig. 2) if the function $w(E, x)$ is known.

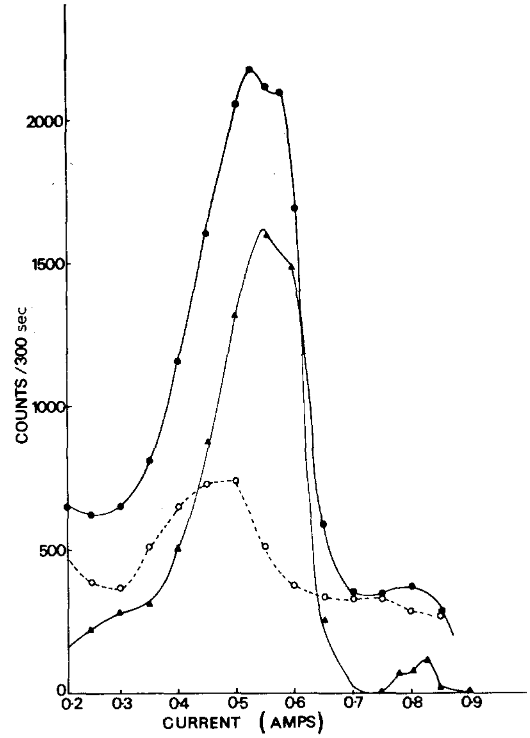

Figure 2 Electron energy spectra obtained from ^{57}Fe-implanted foil on resonance (transducer off) ●, off resonance (transducer on), ○, difference spectrum △.

From our initial studies we conclude that energy resolved ^{57}Fe Mössbauer spectroscopy is a viable technique for the elucidation of the depth distribution of iron-sites in implanted foils. The high quality of the spectra suggests that implant concentrations down to 5×10^{15} implanted atoms $\mathrm{cm^{-2}}$ may be readily studied and experiments are under way to investigate the nature of the implanted species at a variety of concentrations and energy of implantation using energy analysed CEMS.

TABLE I Isomer shifts and quadrupole splitting derived from the energy resolved conversion electron Mössbauer spectra

Spectrometer Setting I(A)	Isomer shift (δ) (referenced to iron foil) (mm sec^{-1})(± 0.004)	Quadrupole splitting (Δ) (mm sec^{-1})(± 0.006)
0.56	0.201	0.507
0.58	0.205	0.508
0.60	0.206	0.520
0.62	0.203	0.525
0.64	0.203	0.521

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Microstructural stability of directionally solidified CoTaC eutectic in a high temperature gradient

At the "Conference on In Situ Composites-II", (Bolton Landing, New York, 1975) the problem of microstructural instability of directionally solidified CoTaC in a high temperature gradient transverse to the fibres was discussed. It appeared that an unexpected and unwanted instability of TaC fibres was responsible for the complete degradation of the composite [1, 2].

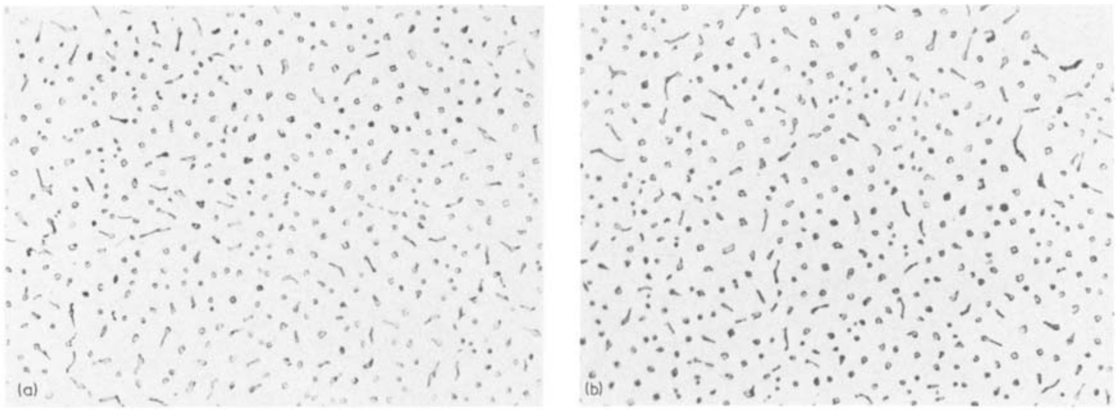

Figure 1 Microstructure of directionally solidified eutectic in a high transverse temperature gradient: (a) as solidified; (b) after 250 h annealing in a temperature gradient of 270 K mm^{-1} at 1383 K maximum temperature.