pagation and the effects produced by the interactions of the compressive and crack tip stress fields are difficult to assess and the results remain as the only anomalies.

The remainder of the results are in close agreement with the measured K_{IC}/crack speed curve [14] and the values are sufficiently consistent to confirm that crack speed/viscoelastic effects are responsible for the observed differences in the literature and re-affirm the validity of linear fracture mechanics applied to this plastic.

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Crystallization behaviour of an amorphous FePC alloy

Rastogi and Duwez [1] have recently reported the rate of crystallization of an amorphous $Fe_{75}P_{15}C_{10}$ alloy (where subscripts indicate the atomic percentages of the respective elements) using thermal analysis, resistivity and X-ray techniques. In the present investigation, the morphology of the crystallites during the early stages of crystallization of this amorphous alloy has been studied using transmission electron microscopy. A detailed description of alloy specimen preparation and experimental techniques is given elsewhere [1, 2].

Preliminary ageing results indicated that the amorphous-to-crystalline transformation below 300°C was not detectable by transmission electron microscopy. On the basis of this observation, annealing experiments were performed at temperatures between 300 and 420°C, in steps of 20°C, with the annealing time at a constant 24 h. A new specimen was used for each of the annealing temperatures. Thin foils were prepared from the annealed specimens using a solution of 10% perchloric acid in ethyl alcohol, maintained at 0°C, and were subsequently examined with a Siemens Elmiskop I electron microscope operating at 100 kV.

Specimens annealed at 300°C indicated the formation of 75Å crystallites of average size by random nucleation in the amorphous matrix. The corresponding electron diffraction pattern consisted of a few broad haloes and was very similar to that of the amorphous alloy. Annealing at 320°C resulted in the formation of spherulite-type microcrystals, as shown in Fig. 1a, and the matrix appeared to be amorphous. The corresponding electron diffraction pattern shown in Fig. 1b suggests that diffraction spots are due to crystallites, while the broad diffraction ring is associated with the amorphous matrix. At 340°C, these crystallites grow in the preferred direction, like dendrites, and this tendency seems to be more pronounced at 360°C (Fig. 1c). The appearance of broad haloes illustrated in Fig. 1d, indicates the presence of an amorphous matrix at 360°C. The analysis of the electron diffraction

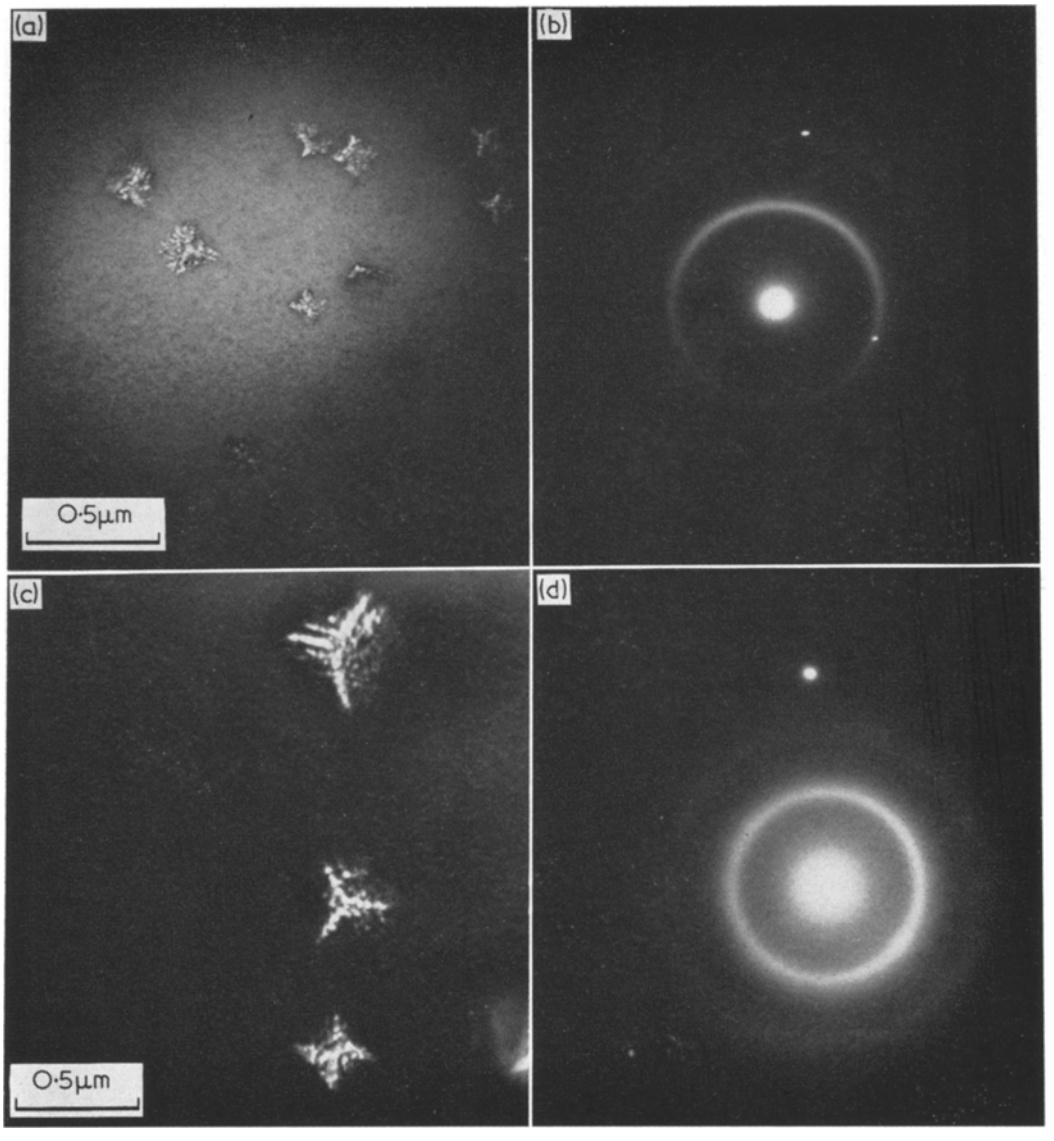

Figure 1 Electron micrographs (a and c) and electron diffraction patterns (b and d) of specimens heated for 24 h at 320°C (a and b) and for the same time at 360°C (c and d).

pattern (not shown) obtained from crystallites shown in Fig. 1c indicates the presence of Fe_2P and α-iron. The microstructure of specimens annealed at 380°C (Fig. 2a) consists of precipitates and an amorphous matrix. These precipitates exibit a lamellar morphology and the analysis of corresponding electron diffraction pattern (Fig. 2b) suggests the presence of Fe_2P, α-iron and Fe_3P phases. After annealing at 400°C, no marked changes in morphology were observed except for the complete transformation of the amorphous matrix into crystalline phases (Fig. 2c). Moreover, the analysis of electron diffraction pattern (Fig. 2d) also indicates the presence of the same phases as those found after annealing at 380°C. The spacing between the lamella at 400°C was estimated to be about 140 ± 20Å.

Since the crystallization process at 400°C was slow, new specimens were annealed at that temperature for 48 and 96 h, respectively. It was found that the specimens heated for 48 h had the

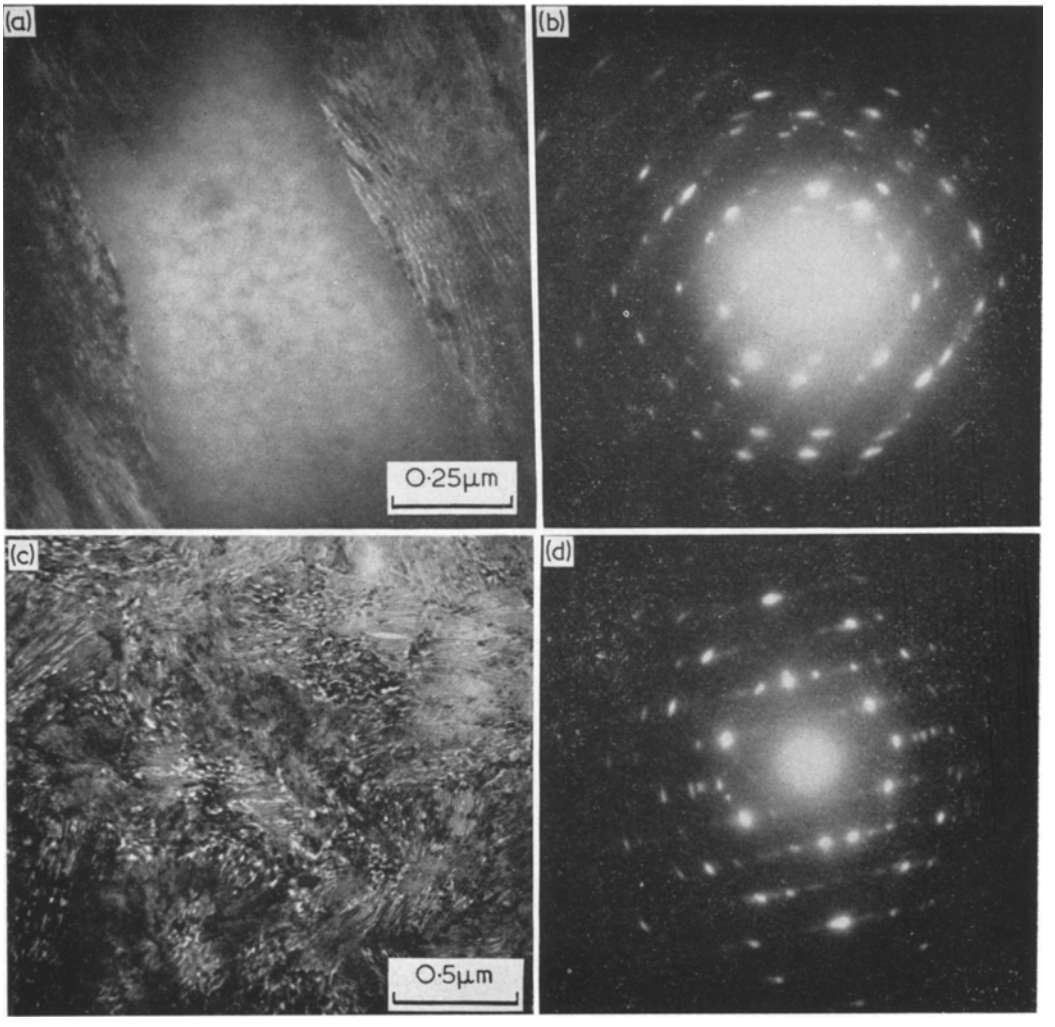

Figure 2 Electron micrographs (a and c) and electrondiffraction patterns (b and d) of specimens heated for 24 h at 380°C (a and b) and for the same time at 400°C (c and d).

same phases as observed in the 24 h annealed sample. A sample annealed for 96 h indicated the formation of cementite and the microstructure consisted of α-iron, Fe_3P and Fe_3C. Upon annealing at 420°C, the microstructure indicated the presence of the same phases which had been detected after the 96 h anneal at 400°C.

The foregoing annealing experiments indicate that during the initial stages of crystallization, very small crystallites are formed in the amorphous matrix. These subsequently grow with a dendritic morphology at higher temperatures as shown in Fig. 1c. Non-uniform rings, as well as layer type diffraction patterns (shown in Figs. 2b and 2d) also indicate that precipitates formed at 380 and 400°C exhibit a strong tendency to grow in preferred directions.

In short, transformation of the amorphous $Fe_{75}P_{15}C_{10}$ alloy to the crystalline phases takes place by the nucleation and growth processes. A similar mechanism has also been reported in various other amorphous alloys [3-8]. The dendritic morphology of crystalline phases consisting of α-iron and Fe_2P in $Fe_{75}P_{15}C_{10}$ alloys first becomes pronounced after annealing at 360°C. The Fe_3P phase is detected upon annealing between 380 and 400°C. After a 96 h anneal at 400°C, Fe_3C is also formed with the micro-

structure consisting of α-iron, Fe_3P and Fe_3C. At 420°C, the above phases are formed and the transformation of amorphous $Fe_{75}P_{15}C_{10}$ alloy to crystalline phases seems to be complete.

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Scanning electron microscopy observations of polyethylene spherulites

It is well known that often when polyethylene and certain other polymers are crystallized from the melt, they form banded spherulites which appear in the polarizing microscope as round or polygonal structures having a black Maltese cross and a series of concentric light and dark rings [1]. The most commonly accepted model for these to date, based almost solely on detailed analysis of the extinction patterns visible in the polarizing microscope [2-6], postulates that banded spherulites are aggregates of ribbonlike folded chain lamellae radiating outward from the centre of the spherulite while undergoing a series of full twists about the radially oriented *c*-axis. This model successfully explains the X-ray evidence [7] for a tangentially oriented *c*-axis as well as the periodic variation in refractive index along the radius necessary to produce the rings. A model of such lamellae is shown in Fig. 1, which shows a set of twisted copper strips whose edges were painted white for emphasis. All twists of the optically uniaxial lamellae must be in phase to produce the bands.

However, the optical evidence is somewhat indirect, depending heavily on the theory of optical extinction and on subtleties of the model being used. The use of the optical microscope is limited by low depth of field and insufficient resolution to see individual lamellae, and electron microscopy of replicas of spherulites [1] has not confirmed unambiguously the existence or nature of the twist. For these reasons, it was decided to use the scanning electron microscope (SEM), where these problems are to a large extent eliminated, to try to clarify the lamellar structure.

Samples 1 to 3 mm thick of melt-crystallized linear polyethylene were prepared by melting pellets of whole Marlex 6015 (M_n = 7500, M_w = 153000) on a glass slide on a hot plate and quenching the slide on an aluminium plate set on top of some crushed ice. The samples showed typical banded spherulites in the polarizing microscope. To enhance the surface relief

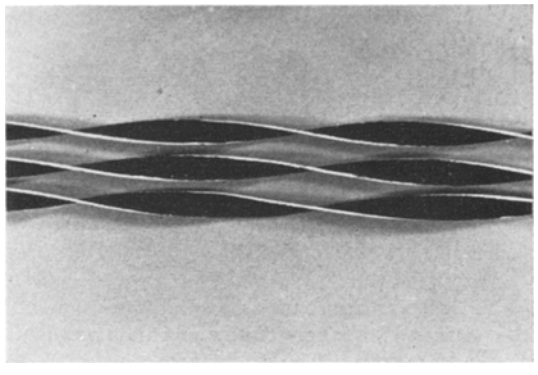

Figure 1 Schematic packing arrangement of lamellae with full helical twists.