this case it appears that both the slope, $m(T)$, and the minimum value of the stress intensity factor, K_m, vary monotonically with temperature. The ratios of slopes at different temperatures may be compared to the inverse ratios of the square roots of viscosities:

$$\frac{m(8)}{m(25)} = 0.61; \quad \left(\frac{\eta(25)}{\eta(8)}\right)^{\frac{1}{2}} = 0.80$$

and

$$\frac{m(15)}{m(25)} = 0.66; \quad \left(\frac{\eta(25)}{\eta(15)}\right)^{\frac{1}{2}} = 0.82.$$

Unlike for the PMMA results, no close agreement is seen, indicating that the temperature dependences of the other factors in $m(T)$ (i.e. of $l_0, \bar{P}, \sigma_y$ and E) may be important also. There is not enough information to separate the various factors, but it is likely that the local yielding properties and the density of microvoid formation are more sensitive to temperature than was the case for the PMMA. The minimum stress intensity factor, K_m, decreases by 37% over the temperature range 8° C to 25° C, indicating that craze initiation is easier (i.e. requires less stress) at the higher temperature.

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Crystallographic relationships arising during the cellular growth of the Cd–Zn eutectic

This work is part of the general study of eutectics which has been in progress in the authors' laboratory for some time. Earlier studies were principally concerned with the development of a characterisation scheme for eutectic morphologies [1–3]. This was followed by a detailed analysis of the mechanical properties of various members of the characteristic morphological groups [4–8]. In one system in particular, Cd–Zn [9], tested in both tension and compression, it was found that the strength of the eutectic composite increased significantly as the specimen growth rate, R, was increased: the ultimate tensile strength (UTS) increased from 107 to 186 N mm^{-2} and the ultimate compressive strength (UCS) increased from 176 to 420 N mm^{-2}. However, the increase in R was accompanied by a decrease in lamellar spacing, λ, and an increase in cellular growth, shown in Fig. 1a, which was found to be particularly pronounced at a growth rate, R, of 4000 mm h^{-1}, the fastest speed used. As a result, it was not clear whether cellular growth, or both of these changes, was responsible for the increased strength.

In the Cd–Zn eutectic, both phases have a close-packed hexagonal structure and grow with $(0001)_{Cd} \| (0001)_{Zn}$ and $[01\bar{1}0]_{Cd} \| [01\bar{1}0]_{Zn}$ [10, 11]. The unit cell dimension c/a ratios for

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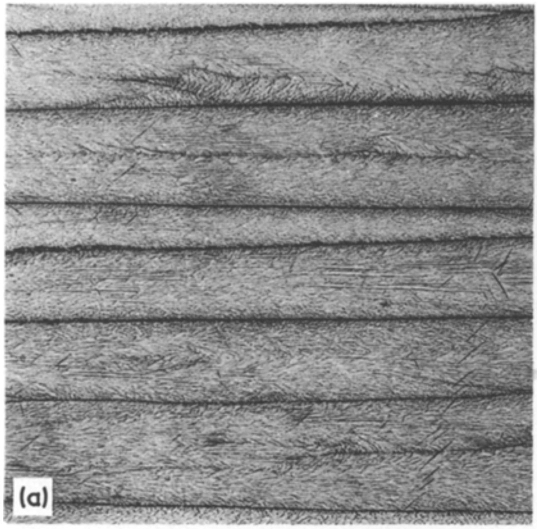

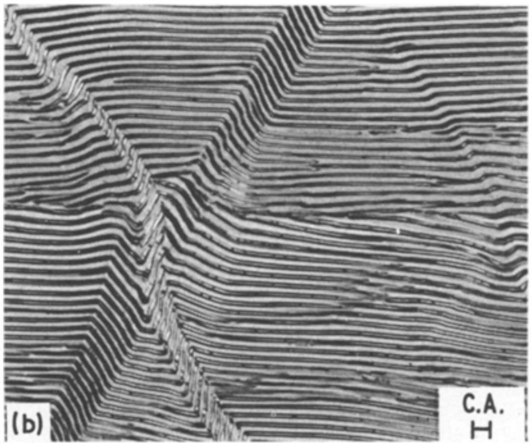

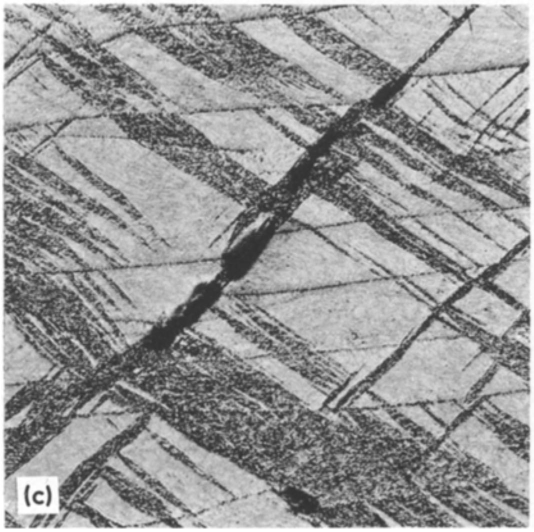

Figure 1 Optical micrograph of longitudinal sections of the directionally-solidified Cd–Zn eutectic (C.A. = compression axis). (a) As-grown, $R = 1600\,\mathrm{mm\,h^{-1}}$ (× 100), (b) Compressed, showing kinks, slip lines and cross-slip patterns, $R = 12\,\mathrm{mm\,h^{-1}}$, strain = 2.5% (× 520), (c) Stretched, showing deformation twins near the fracture surface, $R = 4000\,\mathrm{mm\,h^{-1}}$, fracture strain = 5% (× 300).

the Cd- and Zn-rich phases are 1.886 and 1.856, respectively. The lamellar interface "habit" is $(0\,0\,0\,1)_{\mathrm{Cd,Zn}}$ and so virtually complete epitaxy would be expected across the phase boundary. As a result, the regular lamellar eutectic would be expected to behave almost as a single-phase material. It is seen from Fig. 1b that this appears to be the case [9].

During cellular growth, the solid–liquid interface becomes covered by the well-known cellular projections. The lamellae grow in such a way that the interlamellar boundaries remain perpendicular to the local interface and, as a result, the lamellae "fan out" and thicken as they move away from the centre-line of the cell. To do this, the lamellae must change their habit and/or their orientations. If their orientations change then cellular growth might be expected to promote strengthening, as compared with the regular lammellar eutectic, since many dislocations or sub-boundaries would be required to effect the changes. Transmission electron microscopy has been used to determine if this is the case.

Specimens which had been grown earlier at a growth rate, R, of $4000\,\mathrm{mm\,h^{-1}}$ [9] were prepared for electron transmission microscopy by spark machining to 0.5 mm thickness followed by electro-jet polishing in a (4 vol% HNO_3 + 96 vol% CH_3OH) mixture.

Transmission electron micrographs are shown in Fig. 2 for a specimen grown at $4000\,\mathrm{mm\,h^{-1}}$. The transverse section shown in Fig. 2a is regular and, from the selected area diffraction pattern, it is seen that the lamellar direction is $[0\,1\,\bar{1}\,0]$ and the zone axis is $[2\,\bar{1}\,\bar{1}\,0]$, indicating a $(0\,0\,0\,1)$ habit plane.

As for the longitudinal section, Fig. 2b, it is seen that there is a marked change in lamellar direction across the section. Selected area diffraction at random points (A, B, C and D) on either

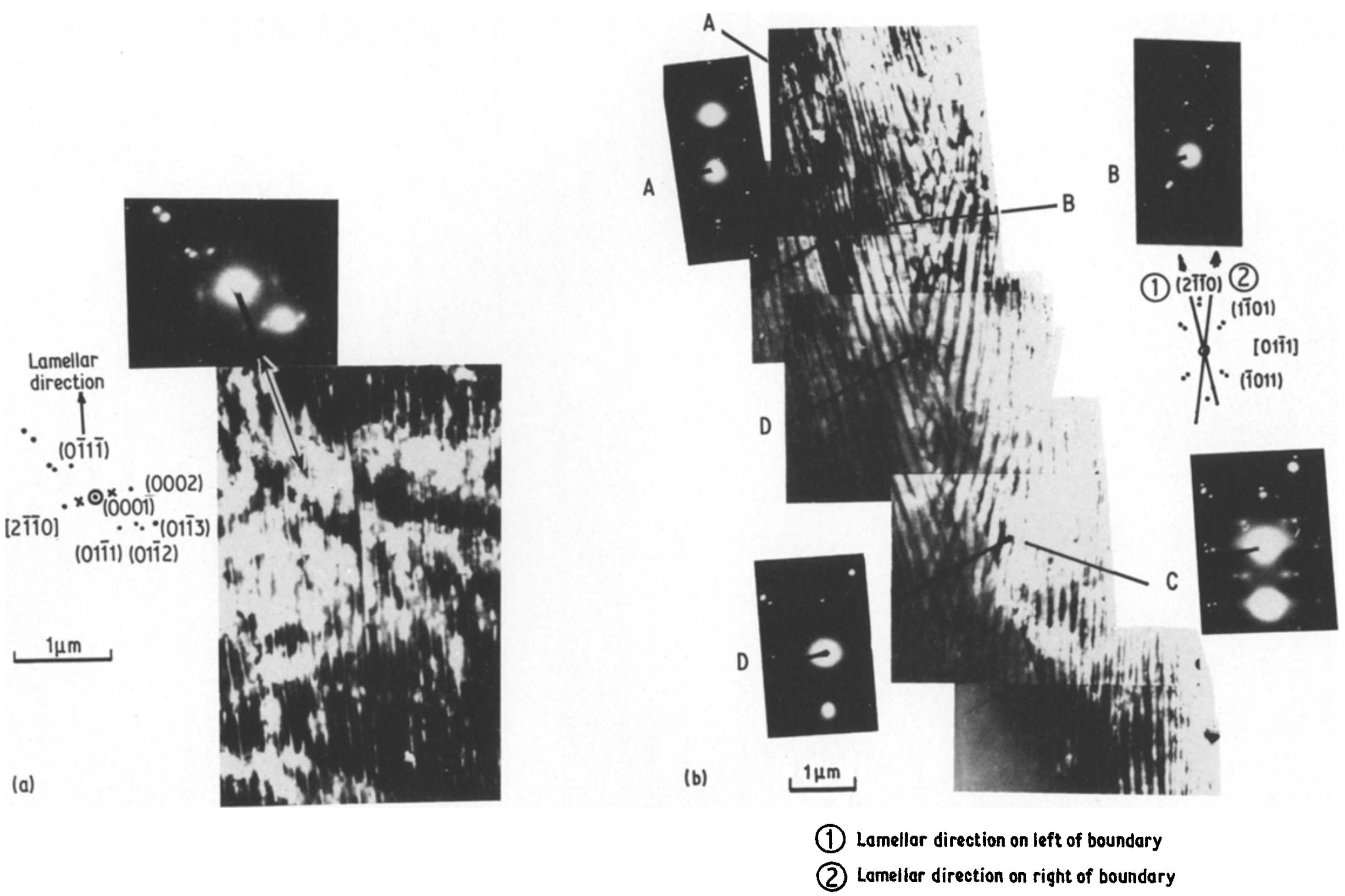

Figure 2 (a) Transmission electron micrograph and selected area diffraction pattern of an area well away from any cell boundaries in a transverse section of a specimen grown at $R = 4000\ \mathrm{mm\,h^{-1}}$. (b) Transmission electron micrograph and selected area diffraction patterns of an area at a cell wall in a longitudinal section of a specimen grown at $R = 4000\ \mathrm{mm\,h^{-1}}$.

side of the cellular boundary give the same zone axis pattern orientation. This indicates that the $[2\bar{1}\bar{1}0]$ crystal direction of each phase is maintained but that the (0001) habit plane is lost in the vicinity of the cell boundary being replaced, in this particular case, by a $(02\bar{2}\bar{5})$ habit.

It is obvious from Fig. 2 that as the solid–liquid interface of the Cd–Zn eutectic becomes cellular the interpenetrating Cd- and Zn-rich crystals continue to grow with a direction $[2\bar{1}\bar{1}0]$ parallel to the specimen axis. However, in those regions near a cell wall, the fanning-out of the lamellae destroys the common (0001) habit. This view is supported by the absence of any appreciable dislocation substructure near the boundary.

Thus it would appear that the cell walls should not provide any appreciable obstruction to dislocation movement during deformation. However, the reason why the deformation twins appear to be halted by cell walls, Fig. 1c and [9], is unclear but the fact that they are implies that there is sufficient mismatch at a cell wall to provide the necessary dislocation "pins". Thus, in the absence of further evidence, it is presumed that the principal cause of the increased strength consequent upon the more rapid solidification of the Cd–Zn eutectic is the decreased interlamellar spacing, but that the minor mismatch associated with cellular growth also contributes to the strengthening.

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Effect of co-polymerization on the relaxation time and molar free energy of activation of polyacrylonitrile

In the previous paper [1], the dielectric relaxation study of polyacrylonitrile (PAN), whose structure is known through X-ray diffraction studies, was reported. The discrepancies in the dielectric relaxation data on PAN in the same range of temperature and frequency were reported by others and have been discussed. A comparative study [2] of relaxation time and molar free energy of activation has also been performed.

In another study [3], the effect of co-polymerization on the crystalline structure of polyacrylonitrile was observed by wide-angle X-ray diffraction studies and a two-phase structure was found to be more suitable to explain the results. A dielectric relaxation study [4] of polyacrylonitrile and its co-polymers with poly-2-hydroxyethyl methacrylate, P(HEMA), also favours the presence of an amorphous phase in polyacrylonitrile.

In this communication the effect of co-polymerization of PAN with HEMA on relaxation time and molar free energy of activation is reported. Homopolymers of PAN and HEMA and random co-polymers, P(AN – HEMA)–I (10% HEMA by weight) and P(AN – HEMA)–II (25% HEMA by weight) were prepared by the method already described [5] with dimethylformamide as solvent and 0.5 mol% α, α' azobis – isobutyronitrile at 60° C in an inert atmosphere.

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