of the short form. The average weight of tall-form crystals was 120 g, while that of the short form was 25 g.

Attempts to display domain configuration on both types of crystals by tellurium evaporation showed that the lenticular domains normally observed in TGS slices were absent. Qualitatively this effect was confirmed by the difficulty experienced in separating cleaved slices from a crystal specimen. The absence of reversely polarized domains would lead to a greater electrostatic attraction due to the enhancement of the surface charges developed on the opposing surfaces of the cleavage.

A Sawyer-Tower hysteresis loop circuit was used to observe any differences between doped and normal TGS crystals. "y"-axis cleavage plates approximately 0.25 mm thick were prepared and gold electrodes of 3 mm diameter were vacuum deposited onto the faces. Comparison with undoped TGS showed no significant difference in the value of spontaneous polarization P_S, but large intrinsic bias was observed in hysteresis loops from both tall and short habit crystals. In addition, about one third of the specimens investigated showed gross deformation of the P/E loops, i.e. pronounced double or triple loops, while one in ten showed slight deformation of the loop.

It is concluded that the addition of alanine induces a growth asymmetry which is not observed in "pure" TGS growth. This observation tends to confirm the work reported on locked-in polarization of alanine doped TGS crystals.

Acknowledgements

Part of this work was supported by a CVD contract and this paper is published by permission of Ministry of Defence (Procurement Executive).

References

1. E. J. WEIDMANN and J. C. ANDERSON, *Thin Solid Films* 7 (1971) 27.
2. P. J. LOCK, private communication.

Received 4 and
accepted 9 February 1972

E. J. WEIDMANN
E. A. D. WHITE
V. M. WOOD
Department of Electrical Engineering
Imperial College of Science and Technology
London, UK

Longitudinal crazing in isotropic polymers

Crazing in isotropic amorphous polymers has been extensively studied and several criteria have been proposed for craze appearance and the orientation of craze growth with respect to the applied-stress field [1-5]. In total, the observation of Sternstein *et al* [2] that "craze growth occurs along a path such that the major principal (tensile) stress always acts perpendicularly to the craze plane" provides an adequate description of the areal development of crazes in unidirectional deformation. We wish to report some unusual, new observations on craze growth in cyclic deformation; these observations indicate that factors other than the applied-stress field can significantly alter criteria for craze formation and growth in nominally isotropic glassy polymers.

Samples of poly(methyl methacrylate) (PMMA), and polycarbonate (PC), were cycled at constant strain-rate between equal strain limits in tension and compression at 77 K; the experimental technique has been discussed elsewhere [6]. Fig. 1 shows a typical low-cycle fatigue fracture surface in PC; two important fracture characteristics are noteworthy. First, the fracture face is smooth and planar, and shows the high reflectivity typical of a surface created by crack propagation through a well-developed pre-existing craze [4]. In other words, prior to crack propagation, crazes grew normal to the stress axis, i.e., in the conventional craze mode, completely across the specimen cross-section. Second, as shown in greater detail in Fig. 1b, a series of concentric ring-shaped markings cover the fracture surface. Fractured samples were sectioned longitudinally (by a technique described in [7]); Fig. 2 shows such a section, and detailed examination established unequivocally that the shorter longitudinal markings (parallel to the stress axis) are, in fact, crazes. The transverse markings are the traces of conventional crazes formed perpendicular to the stress axis. The concentric rings in Fig. 1 mark the

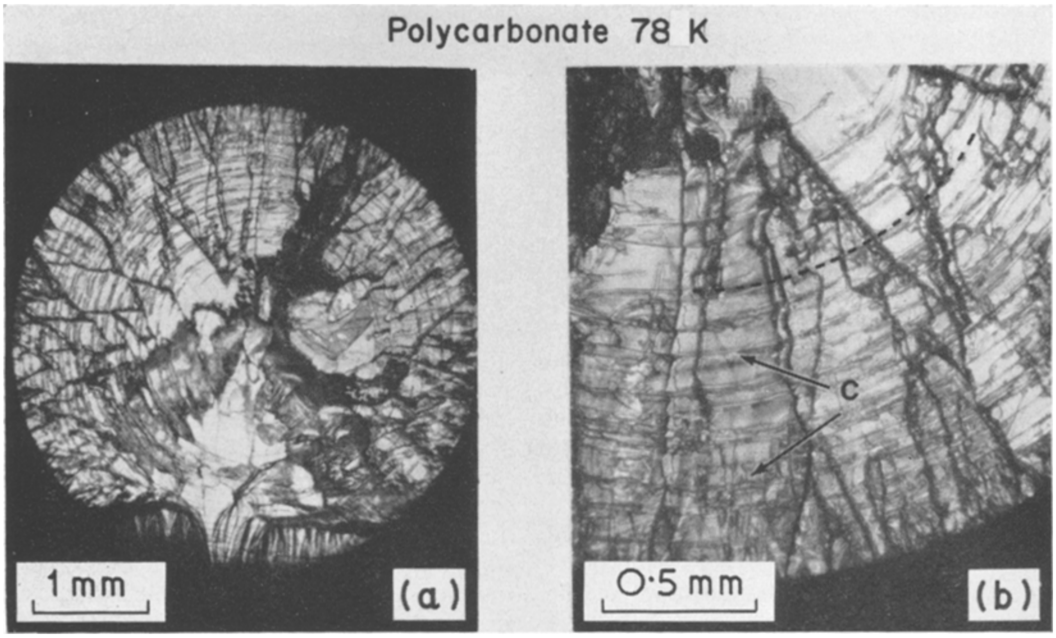

Figure 1 (a) Fatigue fracture surface of PC at 77 K. Note the concentric ring pattern. (b) Higher magnification photograph (two of the concentric rings are indicated by C and one ring is emphasized by the dashed arc).

sites of intersection of annular, longitudinal crazes with the fracture surface. It is emphasized that the orientation of these crazes is *parallel* to the applied-stress axis.

Three characteristics of the longitudinal crazes are noteworthy. First, they are much shorter than the "conventional" transverse crazes, and appear for the most part to originate and terminate at conventional crazes. Second, the lateral spacing between longitudinal crazes appears to be fairly uniform. Third, as seen clearly in the centre of Fig. 2b, when the two craze networks intersect there is a distinct displacement of the longitudinal craze plane. The occurrence of longitudinal crazes, and their general characteristics, are not specific to poly-

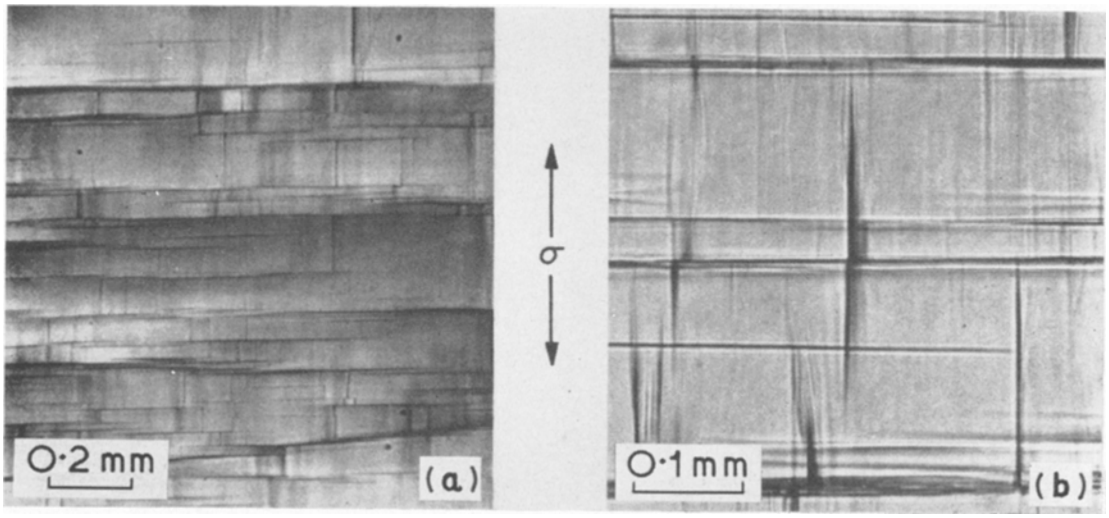

Figure 2 (a) Longitudinal cross-section through the sample of PC shown in Fig. 1. (b) Higher magnification (note the craze intersection in the centre of the photograph).

carbonate; similar observations have been made in PMMA at 77 K, and the phenomenon is believed general to all crazing polymers in cyclic deformation.

One effect of cyclic deformation is to localize non-elastic deformation relative to the more homogeneous deformation obtained in unidirectional testing at the same stress levels. This is analogous to the well-documented localization of plastic strain in fatigued metals [8]. Recent experiments by Wang *et al* [5] indicate that craze formation in glassy polymers is governed by a critical value of the local principal strain or local strain-energy density. Thus, the strain localization associated with cyclic deformation should enhance the propensity for crazing relative to virgin material. In addition, the stress field ahead of a growing craze may be likened, in a qualitative sense, to that of a similarly oriented crack. In particular, as has been shown by Sneddon [9], there is a component of tensile stress *in* the plane of the craze (crack). We suggest that the tensile component of the stress in the plane of the craze, although well below the normal crazing stress, is sufficient to nucleate and grow longitudinal crazes in the intensively strained region at the tip of the growing transverse craze. Fig. 3 is a schematic drawing of the sequence of events believed to lead to the development of the crazes imaged in Figs. 1 and 2. It is known that the conventional transverse crazes grow incrementally through the specimen cross-section on each tensile half-cycle [10]. The longitudinal crazes develop in advance of the growing transverse craze on each tensile half-cycle. The driving force for longitudinal crazing (the tensile stress component parallel to the transverse craze) diminishes rapidly with distance from the transverse craze plane. Thus, the extent of longitudinal craze growth is restricted. In support of this hypothesis, the number of concentric rings on the fracture surface (i.e., the traces of the longitudinal crazes) is in one-to-one correlation with the number of cycles for the transverse crazes to grow completely across the cross-section; the spacing between longitudinal crazes is then dictated by the size of the incremental growth step of the transverse craze.

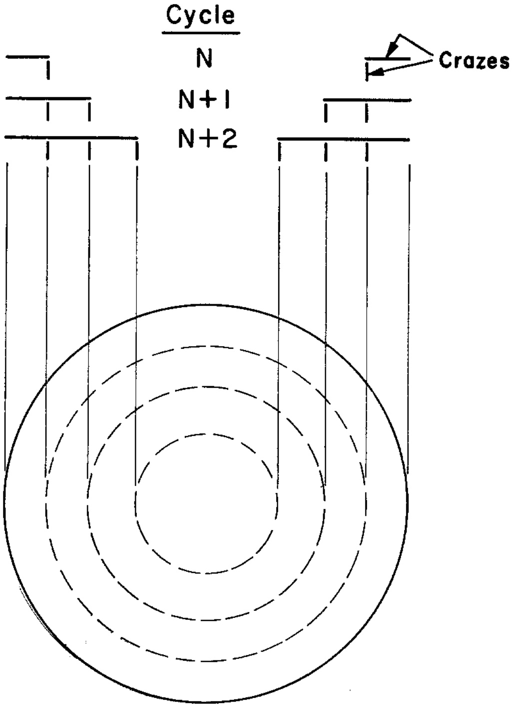

Figure 3 Schematic illustration of the sequence of events leading to the formation of longitudinal crazes.

The unconventional aspect of craze formation and growth described herein emphasizes the incompleteness of current craze growth criteria. In particular, any successful criterion for crazing must eventually incorporate parameters reflecting structural changes resulting from prior deformation, internal stresses and strains, and stress distribution and stress field configuration.

References

1. W. B. KLEMPERER, Theodore von Karman Anniversary Vol., *Appl. Mech. Cal. Tech.* (1941) p. 328.
2. S. S. STERNSTEIN, L. ONGCHIN, and A. SILVERMAN, Applied Polymer Symposia, No. 7 (Interscience, New York, 1968) p. 175.
3. M. B. BEVIS and D. HULL, *J. Mater. Sci.* **5** (1970) 983.
4. S. RABINOWITZ and P. BEARDMORE, *Crit. Rev. in Macro. Sci.*, Chem. Rubber Co. (1972) to be published; also Ford Scientific Laboratory Report No. 71-122.
5. T. T. WANG, M. MATSUO, and T. K. KWEI, *J. Appl. Phys.* **42** (1971) 4188.
6. C. E. FELTNER and M. R. MITCHELL, in "Manual on Low Cycle Fatigue Testing", ASTM STP 465, *Amer. Soc. Test. Mat.* (1969) 27.
7. P. BEARDMORE and S. RABINOWITZ, *J. Mater. Sci.* **6** (1971) 80.
8. D. H. AVERY and W. A. BACKOFEN, in "Fracture of Solids" (Interscience, New York, 1963) p. 339.
9. I. N. SNEDDON, *Proc. Roy. Soc.* A. **187** (1946) 229.

10. S. RABINOWITZ, A. R. KRAUSE, and P. BEARDMORE, *J. Mater. Sci.* to be published.

Received and accepted
25 February 1972

PETER BEARDMORE
STEPHEN RABINOWITZ
Metallurgy Department
Scientific Research Staff
Ford Motor Company
Dearborn, Michigan, USA

Twin morphology in silicon carbide whiskers

Silicon carbide is of interest in many fields of modern technology. In the form of whiskers or filaments it is of possible use as the reinforcing component in fibre-reinforced composites. The high fracture strength and elastic modulus together with the chemical inertness conferred by the surface film of silica, lends the material to this application. The influence of microstructure and crystalline defects on these properties is self evident, and several investigations on this theme have been carried out previously [1-3]. Supplementary results concerning twinning behaviour in silicon carbide whiskers are reported in this publication.

Silicon carbide can exhibit complex crystal structures but is known to exist in its simplest, in the β-cubic (sphalerite) polytype and the hexagonal α-(wurtzite) form. Many more complex hexagonal and rhombohedral structures have been reported, Shaffer [4] having recently reviewed the subject. Optical and electron microscopy [1, 3] has shown silicon carbide whiskers to have a complex morphology although the growth habit appears to be mainly with the axis of whiskers along $\langle 111 \rangle$. Defects in the form of microtwins [1], and contrast bands perpendicular to the whisker axis [2] have been reported previously and explained on the basis of stacking faults or microtwinning on $\{111\}$ planes. Further investigation of defects in silicon carbide whiskers has shown larger twins in both cubic and hexagonal crystallographic forms of the whiskers.

Whiskers of silicon carbide in the form of a close-knit matte were obtained from a commercial source. The matte was cleaned by soaking in HF for 30 min and washed in methanol prior to spreading between the faces of a 100 mesh electron microscope specimen double grid. Treatment with HF removed most of the protective SiO_2 surface film and facilitated penetration of the whiskers by the electron beam. The whiskers were then examined in a Phillips EM 300 electron microscope at 100 kV using a specimen stage having $\pm 6°$ tilt about one axis. Because of the large number of whiskers in any given field of view and the fact that the whiskers grow along primary crystallographic directions, whiskers in a suitable orientation for electron diffraction could be readily found.

X-ray powder diffraction analysis of the whiskers indicated approximately 95% α-phase (6H) to be present in the matte. In view of recent observations made on X-ray intensity of lines from both α and β-phases [5] and conflicting optical results, doubt must be cast on this technique when used with crystallites having a large aspect ratio. Nevertheless, nearly all whiskers which were transparent to the 100 kV electron beam yielded diffraction patterns which could be analysed in terms of the β structure. It is worth noting that the percentage of suitably transparent whiskers was small, $< 2\%$.

Of the SiC whiskers examined very nearly all exhibited defects in the form of stacking faults on $\{111\}$ planes. Van Torne [1] has shown this type of defect to probably be a microtwin of minimum thickness. Also present, but to a lesser extent, were planar defects perpendicular to the whisker axis. These have been shown by Comer [2] to be multiple twins along the $[111]$ axis of the whisker, the twin-matrix relationship being a 180° rotation. Such observations were reported on different material and since the type of defect might be expected to be dependent on growth conditions the observation of both types of defect in one whisker would be somewhat unexpected.

During the present investigation both types of defects were observed in the same whisker, Fig. 4. It can be seen that the central portion of the whisker contains numerous defects on $\{111\}$ similar to those reported by Van Torne [1], whilst the ends of the whisker contains defects perpendicular to the $[111]$ axis of the whisker. This observation would suggest that growth conditions changed slightly during this period of the whisker growth and that nucleation of growth