transferred to a screen grid for electron microscopy utilizing a vacuum tweezer.

Fig. 1 illustrates the stages in preparing isolated sections from a boron-doped (P-type) silicon wafer described above. The preserved surface of one of the isolates is recognized as the surface next to the wax support in the chemical thinning sequence shown in Fig. 1d. In cases where it is desired to examine a section within the wafer bulk away from both surfaces, the procedure involves thinning the isolate from one side for a short period of time, dissolving the wax from the preserved side, and reapplying wax to the polished side. The final polishing is then performed from the preserved surface side. By manipulating the rate of dissolution of the isolate, it is possible to look at the microstructure associated with either surface, or at some estimated depth beneath a surface or between the surfaces. Fig. 2 illustrates somewhat typically the observation of an isolate section in the transmission electron microscope taken from a mechanically polished boron-doped (P-type) wafer. Surface-related defects resulting from precipitation and induced stresses are shown in bright and dark-field electron transmission micrographs.

References

1. R. P. RIESZ and C. G. BJORLING, *Rev. Sci. Instrum.* **32** (1961) 889.
2. G. R. BOOKER and R. STICKLER, *Brit. J. Appl. Phys.* **13** (1962) 446.
3. H. J. QUEISSER, A. H. FINCH and J. WASHBURN, *J. Appl. Phys.* **33** (1962) 1536.
4. J. E. LAWRENCE and H. KOEHLER, *J. Sci. Instrum.* **42** (1965) 270.

W. A. SZILVA
L. E. MURR
M. L. SATTLER
Department of Metallurgical and Materials Engineering,
New Mexico Institute of Mining and Technology,
Socorro, New Mexico, 87801, USA

Fractography of a styrene-acrylonitrile co-polymer—microcracks and band structure

Attention has been given since 1950 to periodic bands which may be observed on the fracture surfaces of glassy polymers [1]. Recently Hull suggested a detailed explanation of their formation in polystyrene. The central idea is that bands are formed by the crack tip jumping into crazes which are generated by its own stress field [2]. Doyle *et al* rejected this idea on the grounds that the bands are formed under conditions where the propagation of the crack tip is too rapid to allow time for extensive craze formation by the mechanism invoked. They offered another explanation which involves periodic detachment of the craze wedge generated ahead of the crack tip [3].

The purpose of the present note is to demonstrate that a banded structure observed on the fracture surface of a styrene-acrylonitrile co-polymer is due to the crack tip jumping into microcracks which are generated in crazes.

The co-polymer was reported by the manufacturer to include 30%, by weight, of acrylonitrile and to have a number average molecular weight of 6×10^4 (Tyril 867; Dow Chemical Company). A powder sample was heated to 180°C and pressed at 84 kg cm^{-2} for 10 min to provide a transparent disc (diameter, 2.7 cm; thickness 0.3 cm). A razor blade was wedged into a saw cut. This resulted in formation of a craze (Fig. 1) which was succeeded by a crack which eventually resulted in fracture of the disc. The fracture surface of the disc included bands irregularly spaced at distances in the range 200 to 800 μm (Fig. 2a). When viewed from the side (along the z-axis in Fig. 1) by reflected light it could be seen that these band spacings correspond to steps on the surface. The detail displayed at higher magnification in Fig. 2b, and designated at its extremes by marks, measures 220 μm.

The progression of the crack tip through the sample could be followed under the microscope as a series of pulses and seemed to fit the "slip-stick" description often used in accounts of the fracture of polymers [4]. At high magnification and low crack speed, of the order 10^{-2} cm sec^{-1}, this process could be followed in detail at the microstructural level. For example Fig. 3a shows the tip of the crack (A), which generated the fracture surface up to this point,
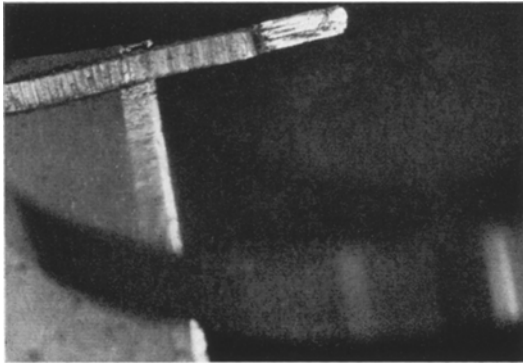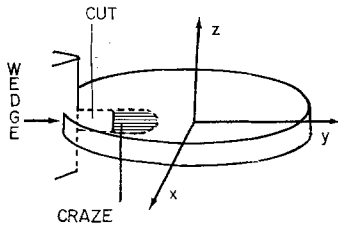
Figure 1 Photograph of razor wedged in cut in disc (× 4), along with diagrammatic representation.

approaching the microcrack (B). The progression of A towards B corresponds to the "stick" stage. When the crack tip A gets close to the micro-crack B (Fig. 3b) a sudden jump is observed as A and B coalesce (Fig. 3c); this corresponds to "slip". The process just described is repeated during progression of the crack throughout the whole sample and accounts for the features shown in Fig. 2.

The formation of microcracks may be attributed to two causes. First, styrene-acrylonitrile co-polymers have a marked tendency to form arrays of approximately parallel crazes when stretched. Previously, an observation of this kind has been made in respect of experiments in which one surface of a sample was put in tension by bending [3]. Second, the crazes readily form microcracks which generally develop from cavities which are formed at the interface between crazed and uncrazed polymer. In most cases the sites of microcrack formation can be located, if not by reference to a positive photograph then to its negative, as being in the region where the craze interface is intersected by some adventitious linear surface defect such as a scratch. For example, in Fig. 3b the two parallel lines indicated by an arrow can be judged to cause cavity formation at the interfaces of a number of crazes which they traverse. This mode of cavity formation was discovered previously in respect of the craze ahead of the crack tip in polystyrene [3]

In general, the present findings appear consistent with a report by Kies *et al* on wedge loading of a number of brittle materials including cellulose acetate, a glassy polymer. "Scallop" markings were observed on the fracture surface which were seen to be formed in a rapid succession of pulses and halts self-controlled by the specimen. George's observations of the creep fracture of an aluminium foil were cited to provide evidence of crack propagation which " . . . consisted of the opening up of advance pinholes in severely strained regions followed by a joining process in which each subsidiary
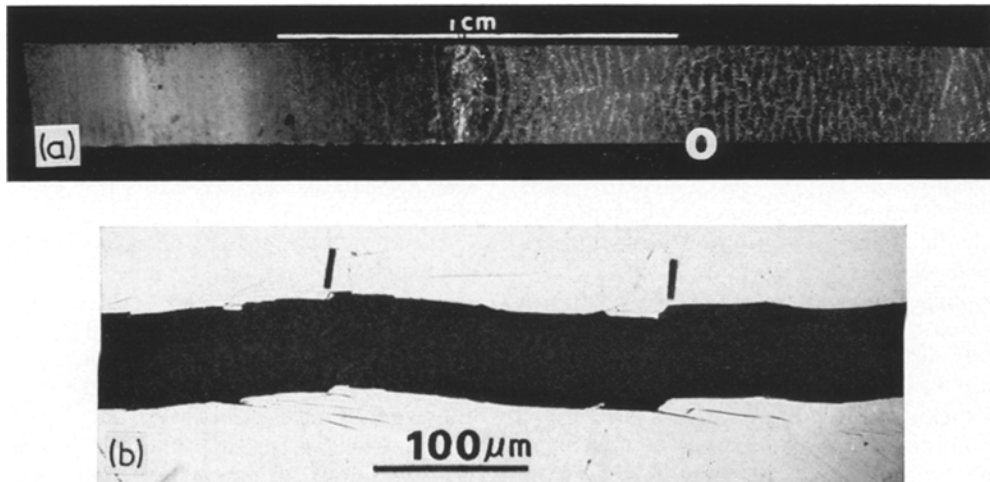

Figure 2 Appearance of fracture surface (a) and magnified side view of a detail (b).
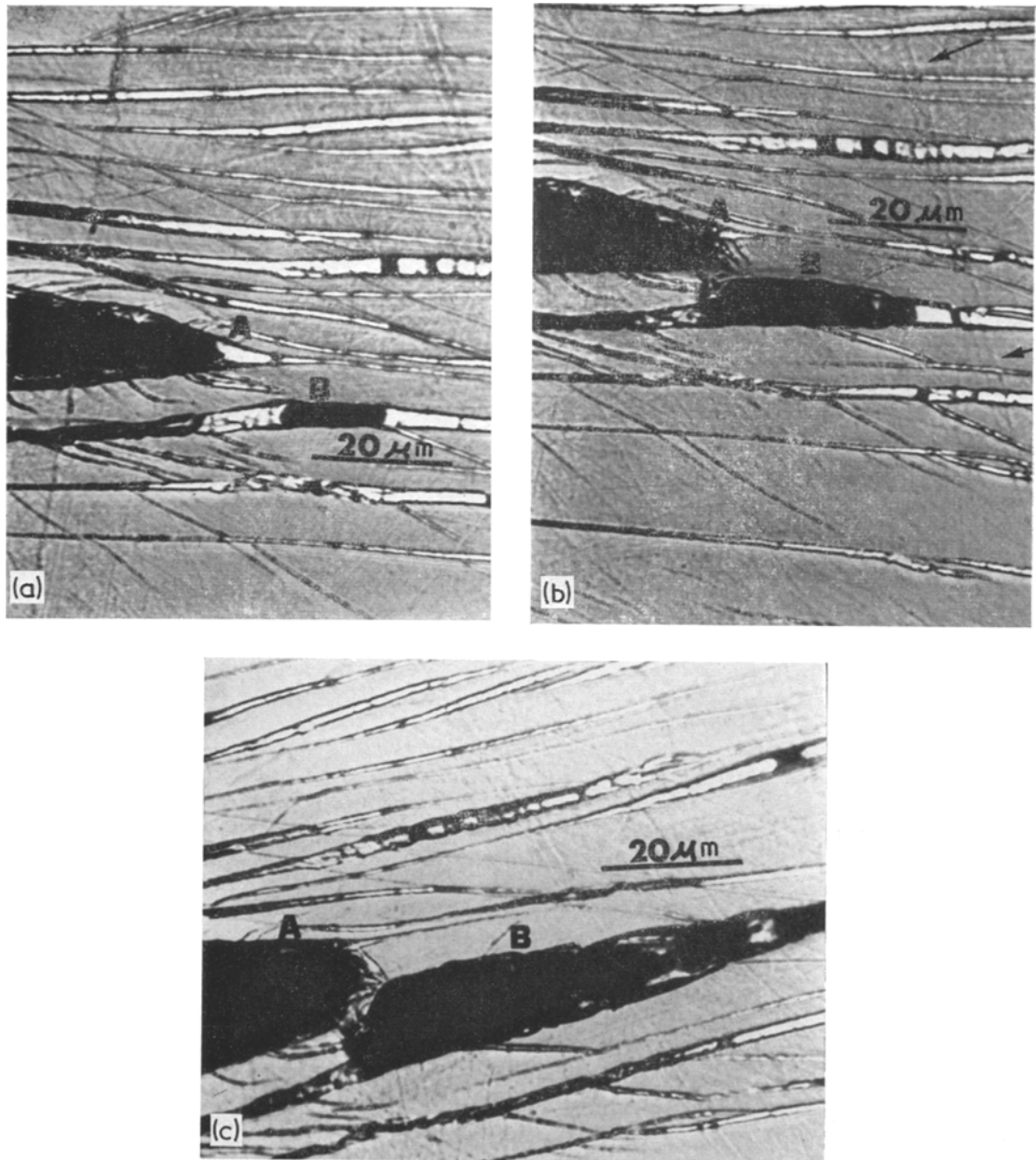
Figure 3 Jumping of crack tip into a microcrack in sequence a, b, and c.

fracture spread backwards as well as forwards". It was concluded that " . . . the propagation of fracture is, in carefully observed cases, essentially and generally discontinuous and consists of the joining up of multitudes of separately initiated components of fracture" [1]. In more detail, the present findings agree with Hull's explanation inasmuch as microcrack formation was observed only in crazes. In addition, the confinement of crazes to the region of crack growth which is evident from observations such as those shown in Fig. 1 is consistent with Hull's suggestion that the crack tip jumps into crazes (or, by the present modification, into microcracks) generated by the stress field of the moving crack tip. However, in order to take account of the criticism of Orowan *et al*, it must be supposed that this stress field differs from that proposed

863

by Hull from consideration of an almost stationary crack tip (cf. [2] and [3]). Experimental clarification of the initiation and propagation of crazes might be possible in the present system by cinematographic studies.

An important final consideration is whether the mechanism of band formation documented here applies to other glassy polymers. Undocumented observations suggest that this is the case for polystyrene. In the case of polymethyl methacrylate craze formation is much less extensive and generally is limited to bifurcation of the craze-crack front. However, the same mechanism of band formation might still apply. A limited documentation for this polymer is to be found in [5].

Acknowledgement

References

1. J. A. KIES, A. M. SULLIVAN and G. R. IRWIN, *J. Appl. Phys.* **21** (1950) 716.
2. D. HULL, *J. Mater. Sci.* **5** (1970) 357.
3. M. J. DOYLE, A. MANCINI, E. OROWAN and S. T. STORK, *Proc. Roy. Soc.* **A329** (1972) 137.
4. E. H. ANDREWS, "Fracture in Polymers" (Oliver and Boyd, Edinburgh, 1968).
5. H. D. MOSKOWITZ, Ph.D. Thesis, Drexel University, Philadelphia, pp. 95-104

H. D. MOSKOWITZ
New York University College of Dentistry,
New York, USA
D. T. TURNER
Dental Research Center,
University of North Carolina at Chapel Hill,
Chapel Hill, N. Carolina, USA

Spin-lattice relaxation of Gd7/2 in calcium tungstate

Previous studies of the relaxation behaviour of rare earth ions in calcium tungstate have suggested [1] that for most rare earth ions the Raman process predominates above about 4.2 K and that only at temperatures below about 2.5 K is the direction process of spin-lattice relaxation dominant. This results in such a large temperature dependent line broadening that the e.s.r. spectra are not generally visible except at low temperatures; in the case of neodymium doped calcium tungstate for example, which has been examined in considerable detail [2, 3] the Nd^{3+} spectrum is only observable around 4.2 K where $T_1 > 1$ msec. No relaxation data appear to have been reported previously, however, for gadolinium-doped calcium tungstate in which, by contrast, all seven main lines of the $Gd^{7/2}$ spectrum are easily observable at room temperature [4, 5].

In the present work, spin-lattice relaxation times were measured using the pulse saturation method at 37.5 GHz. Single crystals of vacancy-compensated gadolinium-doped calcium tungstate, grown by the Czochralski technique, were obtained from the International Research and Development Co Ltd, Newcastle; the nominal gadolinium concentrations were 0.005, 0.01 and 0.05 at. % Gd respectively. In preliminary examinations of the spectra at room temperature it was observed that with the highest concentration crystal the main transitions were sometimes split and that each was accompanied by a number of other lines of weaker intensity. Similar anomalous lines have been reported in cerium-doped calcium tungstate by Klein and Mims [6], who proposed that they were due to local charge compensation in chemically uncompensated material, and in neodymium doped calcium tungstate [7]. Consequently, attention was focused on the 0.005% Gd and 0.01% Gd crystals with which clean single lines were found for each of the seven main transitions at room temperature; even with these however the lines tended to split into two components at 4.2 K, the separation being dependent on the orientation and the gadolinium concentration.

Measurements were made with the magnetic field in the plane perpendicular to the c-axis (i.e. in the ϕ plane) over the temperature range 1.5 to 8 K; the accuracy was ±10%. The observed decay for each line component was a single exponential. The results shown in Fig. 1 refer to the 0.01% Gd sample at $\phi = 10°$, where it was found that the two line components were separated by about 2 mT. Both components showed very similar behaviour and gave exponents of 1.0 and 0.9 respectively. This

864