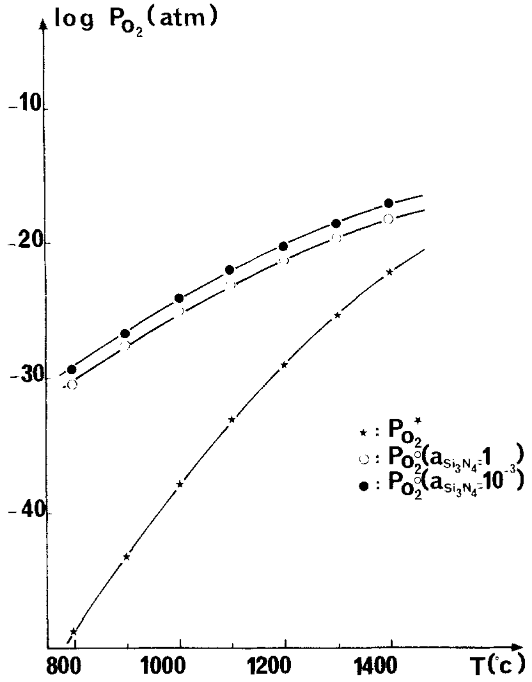

Figure 4 Oxygen partial pressures calculated from Wagner's model ($P_{O_2}^{*}$) [5] and from Gibbs enthalpy for Si_3N_4 oxidation ($P_{O_2}^{\circ}$) [9].

boundary layer and modify the rate of oxygen diffusion through it.

In summarizing the present work is believed to show that a gaseous boundary layer is formed during the oxidation of RBSN in still air. As a consequence, the observed behaviour is closely dependent on sample preparation (porosity, surface finish) and also on the type of furnace used, all factors which may influence the gas flow within the boundary layer and modify the oxygen partial pressure at the gas–solid interface. Apparent kinetics may thus only be valid for given experimental conditions.

Acknowledgements

Thanks are due to J. Canteloup for helpful discussions. Financial support of D.R.E.T. (contract no. 77/435) is also gratefully acknowledged.

References

1. R. W. DAVIDGE, A. G. EVANS, D. GILLINGD and P. R. WILYMAN, "Special Ceramics 5", edited by P. Popper (British Ceramic Research Association, Stoke-on-Trent, 1972) p. 329.
2. S. C. SINGHAL, "Nitrogen Ceramics", edited by F. L. Riley (Noordhoff, Amsterdam, 1977) p. 607.
3. M. E. WASHBURN and H. R. BAUMGARTNER, Proceeding of the Second Army Materials Technology Conference, Hyannis, Massachussets (1973).
4. P. WALZER, M. LANGER and J. SIEBELS, *Z. Werkstofftech.* 8 (1977) 294.
5. C. WAGNER, *J. Appl. Phys.* 29 (1958) 1295.
6. J. W. HINZE and H. C. GRAHAM, *J. Electrochem. Soc.* 123 (1976) 1073.
7. J. P. TORRE and A. MOCELLIN, *J. Mater. Sci.* 11 (1976) 1725.
8. J. SCHLICHTING and L. J. GAUCKLER, *Powder Met. Int.* 9 (1977) 36.
9. O. KUBASCHEWSKI, Ll. E. EVANS and C. B. ALCOCK, "Metallurgical Thermochemistry" (Pergamon Press, Oxford, 1967).
10. J. P. TORRE and A. MOCELLIN, "Nitrogen Ceramics", edited by F. L. Riley (Noordhoff, Amsterdam, 1977) p. 63.

Received 11 April
and accepted 12 May 1978.

P. BARLIER
J. P. TORRE
Centre des Matériaux, Ecole des Mines de Paris
B.P. 87, 91003 Evry Cédex, France

Measurement of craze density by quantitative transmission electron microscopy

The density of crazed matter has generally been measured by Kambour's [1, 2] method of total internal reflection. This technique has the disadvantage that it averages over quite large craze volumes so is not suitable for measuring the variation of density along a craze or the density near the tip of a craze. These densities are of interest because it is not clear how crazes grow in width. They are thought to grow by a combination of crazing new material and elongating the pre-existing craze. Beahan *et al.* [3] suggested from electron microscope observations on polystyrene that the majority of craze width growth is by crazing new material but they did observe a change in morphology as the craze neared its maximum width.

The purpose of this letter is to describe an electron microscope technique for measuring the density of small volumes of crazed matter and to present results obtained with this technique on the variation of density along a craze in polystyrene.

Crazed polystyrene specimens were prepared by the method described by Beahan *et al.* [3]. Thin films were cast on glass from a 2% solution of polystyrene (Dow Styron 685) in toluene. These films were floated into water and picked up on a microscope grid which was then strained manually using tweezers. The specimens were mainly made rapidly with no attempt to evaporate off all the toluene before straining, as the presence of solvents facilitates crazing. One specimen however was dried in a vacuum oven at 70° C for 12 hours before elongation. Some specimens were stripped from their grids and refloated onto water to permit them to relax. This was done using a concentrated solution of polyacrylic acid in the conventional manner. After relaxation for a few hours the specimens were picked up in fresh grids for examination. The films were probably of similar thickness to those studied by Beahan *et al.*, an estimate of their thickness will be discussed later.

The density of crazes was measured using mass thickness contrast in the electron microscope [4]. This technique has been frequently used in quantitative microscopy of biological samples [5, 6]. The microscope is carefully focused to eliminate any significant phase contrast and an objective aperture is used. Under these conditions if the thickness is not too great [6, 7] the intensity on the image plane is given by

$$I = I_0 e^{-Qt}$$

where t is the specimen thickness, Q is the product of atomic cross-sections and specimen density and I_0 is the intensity on the image plane without a specimen. The atomic cross-section employed relates to the probability of an electron being scattered to such an angle that it will not pass through the objective aperture. On the assumption that the thickness of a craze and of adjacent non-crazed material is the same, the relative density (ρ_r) of crazed and non-crazed material is given by

$$\rho_r = \ln \frac{I_{\text{craze}}}{I_0} \Bigg/ \ln \frac{I_{\text{non-craze}}}{I_0}$$

The intensity on the image plane was measured using a photomultiplier which integrated over an area of specimen controlled by the magnification. At the largest magnification this area was a circle of 40 nm diameter. It was important to check that the craze image was larger than the photomultiplier window and this was done photographically. The effects of specimen sublimation and contamination have been examined by a number of workers [6, 8] and found to be insignificant at reasonably low beam currents.

The density measured should be independent of the objective aperture and this was checked using the four aperture sizes (20, 40, 60, 120 μm) supplied on the microscope, a JEM 100C. The results obtained were the same within 5%, which is as good as could be expected considering the accuracy of the photomultiplier meter and calibration. The technique was also checked by operating the microscope in selected area diffraction mode with a wide craze and long camera length so that the photomultiplier collected only electrons scattered with a scattering vector $s[= 4\pi \sin(\theta/2)/\lambda]$ less than 0.8 Å^{-1}. The theory is identical to that described for use of the microscope in the imaging mode and the results obtained agreed within experimental error.

The implicit assumption, that the diffraction pattern of a polystyrene craze is the same as that of non-crazed material, was also examined experimentally and found to be correct for radiation damaged materials such as the films used in this work. A study of the structure of crazed material by electron diffraction is continuing and will be published at a later date.

Hall and Inoue [9] have measured electron scattering cross-sections for polystyrene spheres and used an expression

$$I = I_0 e^{-Sw}$$

where S is the scattering cross-section and w the amount of material in g cm^{-2}. They find, for a minimum scattering angle of 4.4×10^{-3} radians, that $S = 4.5 \times 10^4\ \text{cm}^2\ \text{g}^{-1}$. The absolute thickness of specimens can therefore be measured if an equivalent objective aperture is used. The specimens were found to have a thickness in the range of 50 to 200 nm.

The relative density of crazed matter was measured at six positions in two different crazes in one specimen, in each case the craze width varied from 75 nm minimum to 2200 nm maximum. In addition the density was measured across the wide craze using a probe of 40 nm effective diameter. All those relative craze densities came within the range of 0.30 ± 0.03, so there was no evidence of density variation along or across the craze. The dried specimen has a relative craze density of 0.24 ± 0.03 and the relaxed specimen a density of 0.30 ± 0.03.

The values of craze densities are to be compared with a value of 60% found by Kambour. More recently Doyle [10] has measured densities of the craze layer on fracture surfaces in polystyrene. He used both optical techniques similar to Kambour and also measured the thickness (width) of craze layers before and after collapse. In all cases his values of relative craze density were between 23% and 35%. Krenz *et al.* [11] measured the densities of ethanol-induced crazes in polystyrene by Kambour's method and found a value of 30% ± 10%. It appears therefore that the values of craze density measured on thin films in the electron microscope are in reasonable agreement with other measurements of craze density in polystyrene. Beahan *et al.* [12] has shown that the morphology of crazes in thin films is the same as that in bulk material.

The lack of variation in density along a craze is evidence that the particular craze grew in width from 75 nm to 2200 nm entirely by crazing new material. In addition no evidence was found of a variation of density across a craze. This is perhaps not surprising as in this material no centre line of voids was visible.

The observation that crazes in polystyrene show little tendency to relax is in agreement with the observations of Beahan *et al.* on polystyrene that craze fibrils do not relax after fracture. Bucknall [13] on the other hand quotes considerable evidence for craze recovery after unloading in rubber toughened styrenic materials. In PMMA, Brown and Ward [14] and also Weidmann and Döll [15] found evidence of considerable relaxation of crazes at crack tips. The latter authors, however, found that this degree of contraction of craze fibrils in fracture was molecular weight dependent and quite small for low molecular weight materials.

The conclusions reached were as follows. The density of craze matter can easily be measured by the techniques of quantitative transmission electron microscopy and the results obtained agree well with some measurements of densities of crazes in bulk material. Also crazes grow in width by voiding new material and no evidence was found for width growth by the stretching of crazed matter.

References

1. R. P. KAMBOUR, *Nature* **195** (1962) 1299.
2. *Idem, J. Poly. Sci. A* **2** (1964) 4159.
3. P. BEAHAN, M. BEVIS and D. HULL, *Polymer* **14** (1973) 96.
4. R. D. HEIDENREICH, "Fundamentals of Transmission Electron Microscopy" (Interscience, New York, 1964).
5. R. E. BURGE in "The Interpretation of Ultrastructure" edited by F. E. Lehman (Academic Press, New York, 1962).
6. E. ZEITLER and G. F. BAHR, *Lab Inv.* **14** (1965) 946.
7. L. Reimer and H. Gilde in "Image Processing and Computer-aided Design in Electron Optics" edited by P. W. Hawkes (Academic Press, London 1973).
8. J. W. EDIE and U. L. KARLSSEN, *J. de Microscopy* **13** (1972) 13.
9. C. E. HALL and T. INOUE, *J. Appl. Phys.* **28** (1957) 1346.
10. M. J. DOYLE, *J. Mater. Sci.* 8 (1973) 1185.
11. H. G. KRENZ, E. J. KRAMER and D. G. AST, *ibid.* **11** (1976) 2211.
12. P. BEAHAN, M. BEVIS and D. HULL, *ibid.* 8 (1972) 162.
13. C. B. BUCKNALL, "Toughened Plastics" (Applied Science, London, 1977).
14. H. R. BROWN and I. M. WARD, *Polymer* **14** (1972) 587.
15. G. W. WEIDMANN and W. DÖLL, *Colloid Poly. Sci.* **254** (1976) 205.

Received 12 April
and accepted 26 May 1978.

H. R. BROWN
Department of Materials Engineering,
Monash University,
Clayton, Victoria 3168,
Australia