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Microstructure of glass fibre-reinforced cement composites

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The microstructure and fracture surfaces of glass fibre-reinforced cement (grc) composites have been examined by scanning electron microscopy. The toughness of grc stored in dry environments is attributed to the formation of a complex structure of subsidiary cracks, resulting in a large failure surface area, and the pull-out of the glass fibres. The reduction of the toughness of grc stored in wet conditions over a period of time reflects the reduction in the amount of subsidiary cracking and fibre pull-out. Observations indicate that this is due to changes in the microstructure of the matrix in and around the fibre bundles.

1. Introduction

The relatively high toughness of glass fibre cement (grc) compared to that of cement paste has been attributed to the amount of fibre pull-out resulting from the low bond strength between the glass fibres and the matrix [1]. After prolonged exposure to wet environments grc loses much of its toughness and its strength is also reduced considerably [1]. This is associated with a decrease in the amount of fibre pull-out due to a combination of a weakening of the fibres by alkali attack and an increase in the bond strength. The development and use of alkali-resistant glass fibres (e.g. Cem-FIL*) has improved the durability of grc stored in wet conditions, but eventually the toughness is reduced to low levels.

The scanning electron microscope (SEM) has been used previously to examine the fracture surfaces of grc composites [1, 2]. A recent study [2] has shown that the fibre-matrix interface in the "young" materials, containing Cem-FIL fibres is very porous and consists of loosely bonded, partially hydrated, grains of cement in contact with the fibres. The density of the interface increases with time of storage in water and becomes almost fully dense after a few years when the pores at the interface and the spaces between the fibres in a strand become filled with $Ca(OH)_2$ crystals and other products of cement hydration.

This work concerns the microstructure of grc which has been stored in dry and wet environments for up to 5 years. Detailed studies of the fracture surfaces, the fibres and the fibre–matrix interfaces have been carried out in an attempt to elucidate the modes of failure of the composite and the reasons for its loss of strength in wet environments. It should be appreciated, however, that grc is a generic name given to a wide range of cement composites reinforced by glass fibres and the present study was limited to only one such composite containing one particular form of an alkali-resistant glass fibre.

2. Experimental procedures

The samples of grc used in this investigation were taken from boards manufactured by the spray-suction process [3] at the Building Research Station. This technique employs a glass-chopper mounted on a spray-gun attached to a slurry pump. The cement slurry and streams of chopped fibre strands meet and are sprayed onto a perforated mould; excess water is then removed by suction. The individual fibres are loosely bonded into bundles or strands each containing about 200 separate glass filaments, of approximately 10 μm diameter. The short bundles are randomly orientated parallel to the plane of the board forming a

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TABLE I Details of grc specimens examined by SEM

Board no.	Sample no.	Storage prior to testing	Storage time	Storage after testing
BP 30	88	Water 20° C	90 days	Lab. air
BP 30	69	Nat. weather	1 year	Lab. air
BP 76	23	Water 20° C	90 days	
BP 77	105	Water 20° C	90 days	Lab. air
BP 77	12	Air, 40% r.h.	90 days	
BP 78	71	Air, 40% r.h.	90 days	
BP 112	9	Air, 40% r.h.	90 days	vacuum
BP 112	60	Air, 60% r.h.	90 days	vacuum
BP 112	75	Air, 90% r.h.	90 days	vacuum
OD	10	Water 20° C	5 years	Lab. air
OH*	285	Water 20° C	5 years	Lab. air
OH	–	Air, 40% r.h.	5 years	Lab. air
OH	226	Nat. weather	5 years	Lab. air
OE	232	Nat. weather	5 years	Lab. air
OE	246	Water	5 years	Lab. air
OE	159	Air, 40% r.h.	5 years	Lab. air

W/C nominally 0.3 for all samples.
All samples contained ~ 4 vol % Cem-FIL fibre.
* Contains ~ 10% inert filler.

two-dimensional array of reinforcing fibres. The composites discussed in this paper have a nominal fibre content of 4 vol% and the fibres were 34 mm long. The water/cement ratio of the composites was nominally 0.3.

Specimens were cut from broken mechanical test specimens, the details of which are given in Table I. Some test specimens were kept in laboratory atmospheric conditions for up to 1 year after testing, others were dried in vacuum after testing and then stored under vacuum until required.

The specimens were mounted onto standard SEM aluminium stubs; the specimens and stubs were coated with a thin layer of vacuum-deposited carbon. SEM studies were carried out using a Cambridge Stereoscan Mark IIa coupled to an energy dispersive X-ray spectrometer (EDS), an EDAX model No.707. This combination can provide electron micrographs of the surfaces of the composites combined with qualitative or semi-quantitative analyses of selected regions.

Semi-quantitative analyses of glass fibre surfaces were carried out using techniques developed at BRS [4]. The glass fibres were extracted from the grc samples, some were washed in dilute HCl to remove traces of cement adhering to the fibres and others were analysed without washing. Virgin fibres were washed in acetone to remove the size from the fibre strands. The fibres were mounted on SEM stubs on which had been fixed a disc of pure carbon, using a conducting silver dag.

Values of the SiO_2/ZrO_2 in the glass surfaces were obtained from the calibration curves in Fig. 1 due to Rayment [4]. These curves were obtained by analysing glasses of known $SiO_2/(SiO_2 + ZrO_2)$ and $ZrO_2/(SiO_2 + ZrO_2)$ ratios using the EDS. The analyses were carried out on the basis of count ratios, which were expressed as the proportion of the peak integral corresponding to Si or Zr to the sum of the peak integrals of Si and Zr. Variations in specimen surface geometry with respect to the incident beam and EDS detector precluded the use of count rates for analysis. Care was taken, however, to ensure that the stubs were kept at an angle of 45° with respect to the electron beam and that the line of sight from the area of analysis to the detector was unrestricted. The peak integrals were obtained after smoothing and background subtraction using a dedicated computer linked to the EDAX system. Similar procedures were adopted for the analysis of the glass fibres.

3. Results

3.1. Fracture surfaces

The fracture surfaces of grc stored for 90 days, 1 and 5 years in wet environments are shown in Figs. 2 to 4, and the fracture surfaces of materials stored in dry air for 90 days and 5 years are illustrated in Figs. 5 and 6. Several features of the surfaces are immediately apparent. Firstly the fibre strands are essentially integral in all samples and can, therefore, be considered as the reinforcing element. The amount of fibre pull-out in wet stored grc has decreased with the time of storage, and after 5 years there is little or no pull-out, most fibres failing at one or the other of the fracture faces. By contrast the amount of pull-out has not decreased in dry air stored specimens.

The fracture surfaces of air stored grc are characterized by the large amount of subsidiary cracking which occurs during failure, resulting in a large fracture surface area. The amount of subsidiary cracking decreases with storage time in the wet stored materials. The primary crack which is responsible for the ultimate failure of the composite may result from the intersection of these subsidiary cracks of which there are three types: (a) multiple transverse cracks, which run nearly parallel to the primary crack surface, i.e. perpendicular to the applied tensile stress; (b) matrix shear cracks, running parallel to the applied stress and the plane of the two-dimensional array of glass-fibres; and (c) interfacial cracks observed

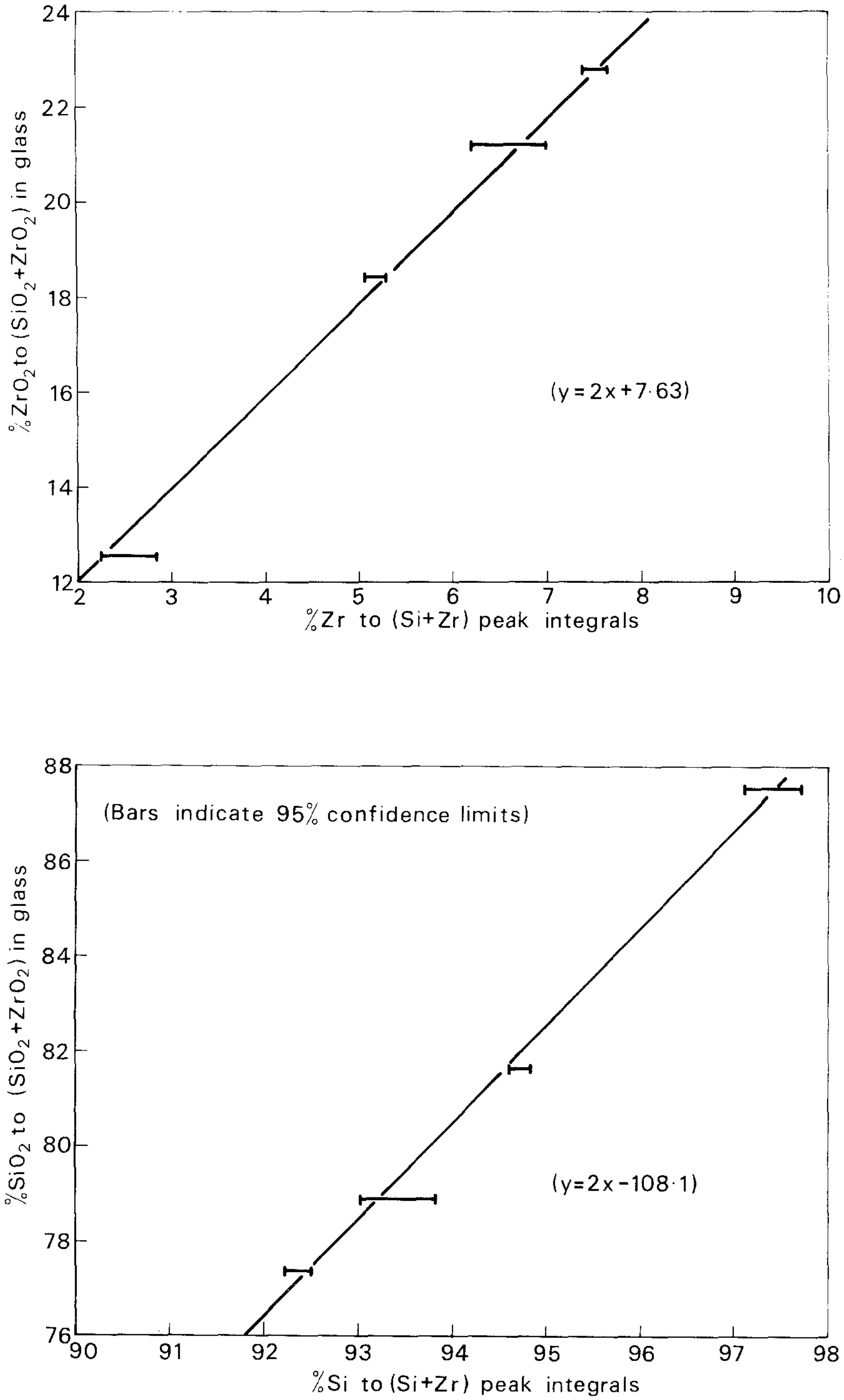

Figure 1 Calibration curves for the analysis of glass fibres using glass standards [4].

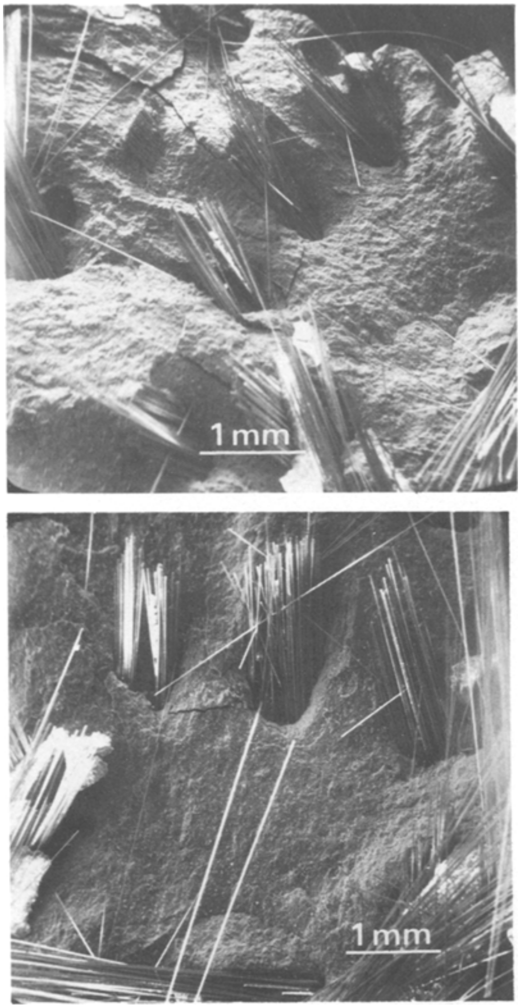

Figure 2 Fracture surfaces of grc stored for 90 days in moist air (90% r.h.) at 20° C.

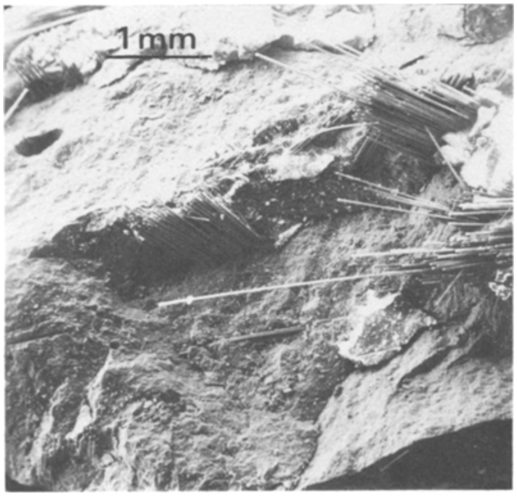

Figure 3 Fracture surface of grc naturally weathered for 1 year.

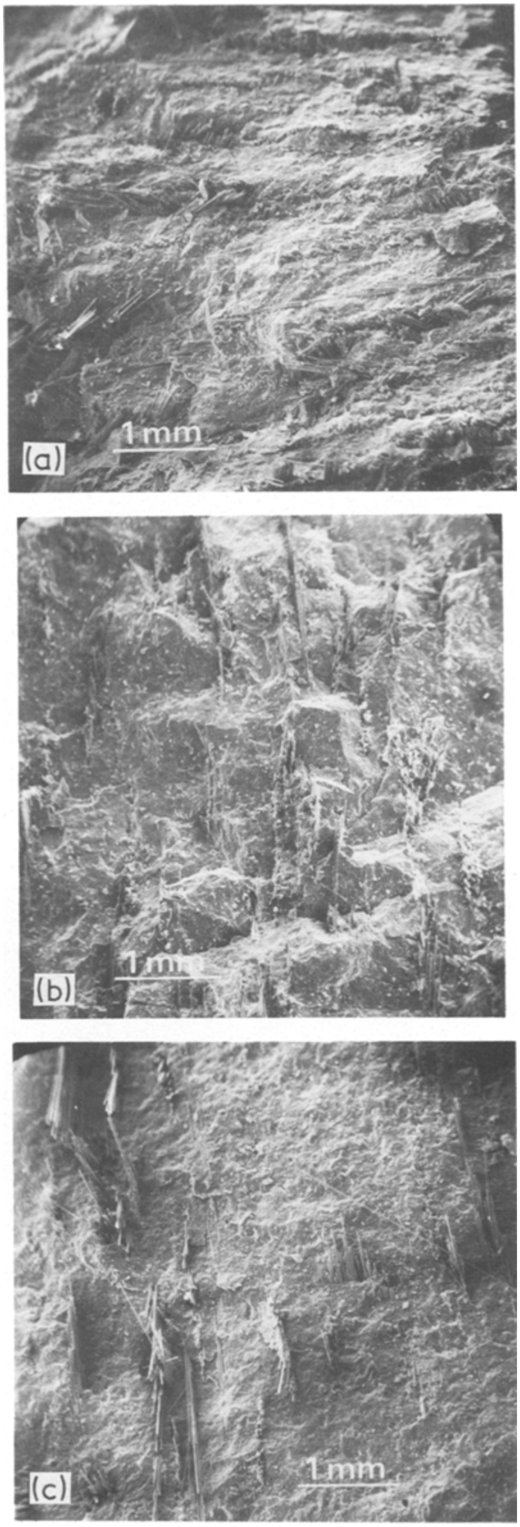

Figure 4(a) and (b) Fracture surfaces of grc stored for 5 years in water at 20° C. (c) Fracture surface of grc naturally weathered for 5 years.

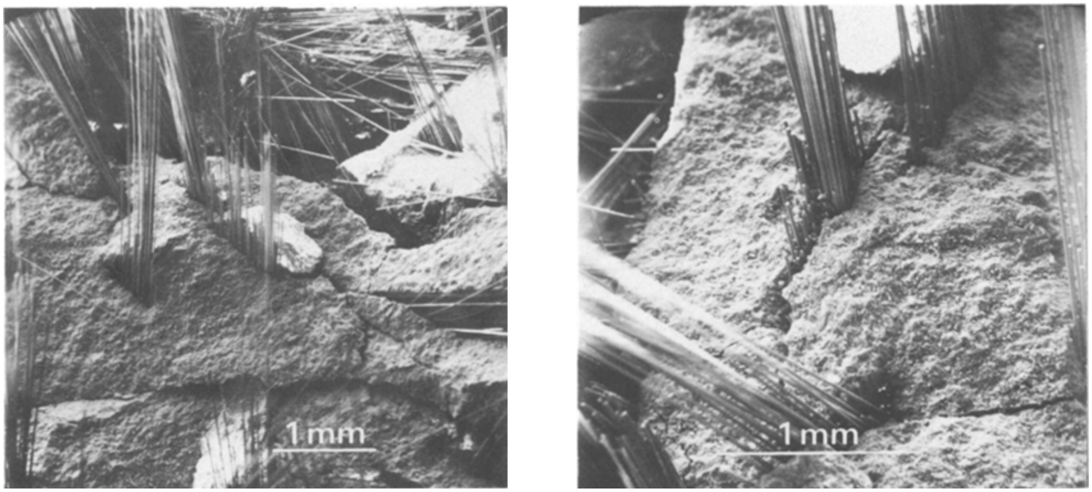

Figure 5 Fracture surfaces of grc stored for 90 days in dry air (40% r.h.) at 20° C.

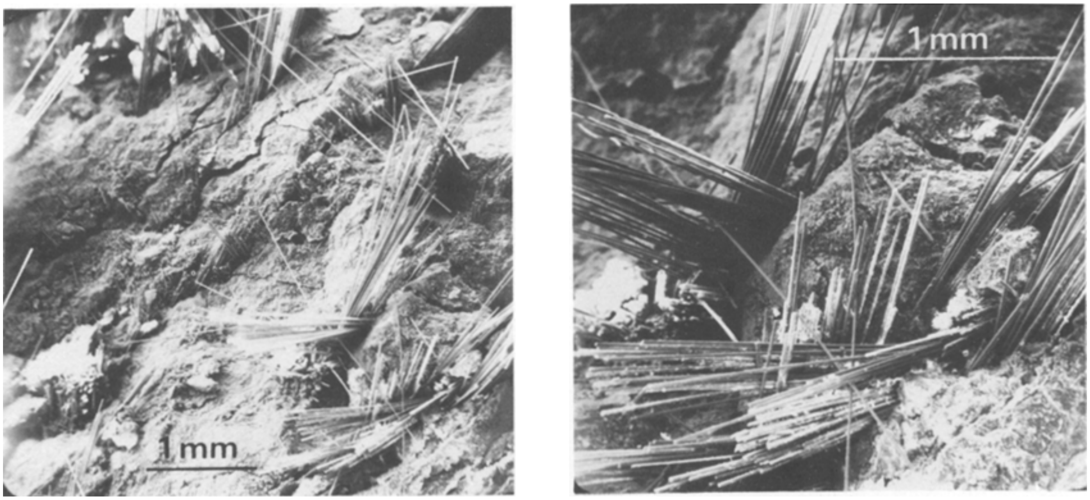

Figure 6 Fracture surfaces of grc stored for 5 years in day air at 20° C.

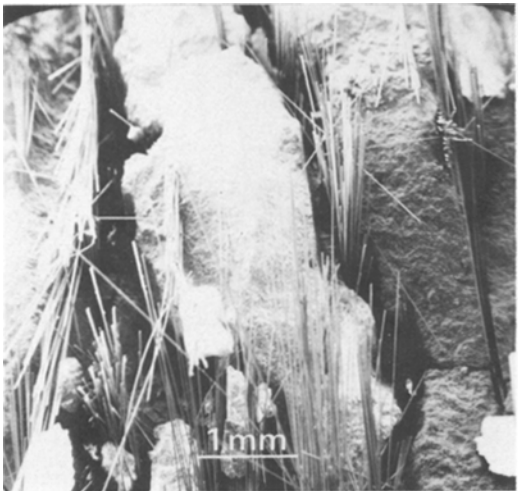

Figure 7 Delamination in grc stored for 90 days in dry air resulting from the linking of interfacial cracks with matrix shear cracks.

around each fibre bundle, resulting from the failure of the fibre–matrix bond and pull-out of the fibres. These cracks are often linked by matrix shear cracks and produce delamination of the composite (Fig. 7).

The amount of subsidiary cracking is reduced in materials stored for long periods in wet conditions. The fracture surfaces of the 5 year water stored and naturally weathered grc are almost planar, with little or no evidence of subsidiary cracking, although some limited shear failure of the matrix around the fibres bundles is observed.

In the 90 day, air stored grc samples some fragmentation or crumbling of the matrix around the fibre strands has been observed (Fig. 8a), resulting in the removal of a wedge shaped section of the matrix. It is also apparent that the fibres within a bundle are quite "loose", the cement

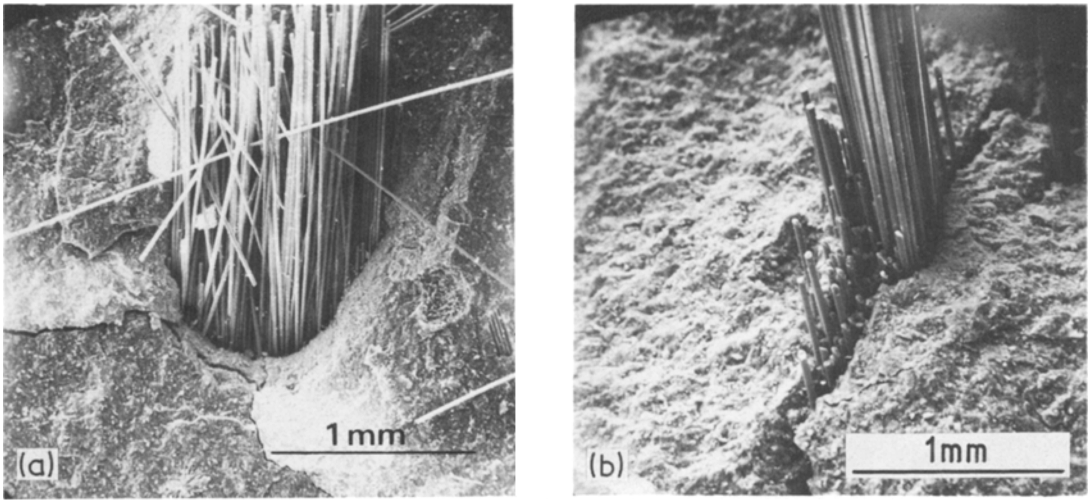

Figure 8 Pulled out fibre strands 90 day grc showing fibre failures at crack surface in flattened strands (a) and matrix crumbling around fibre strand (b).

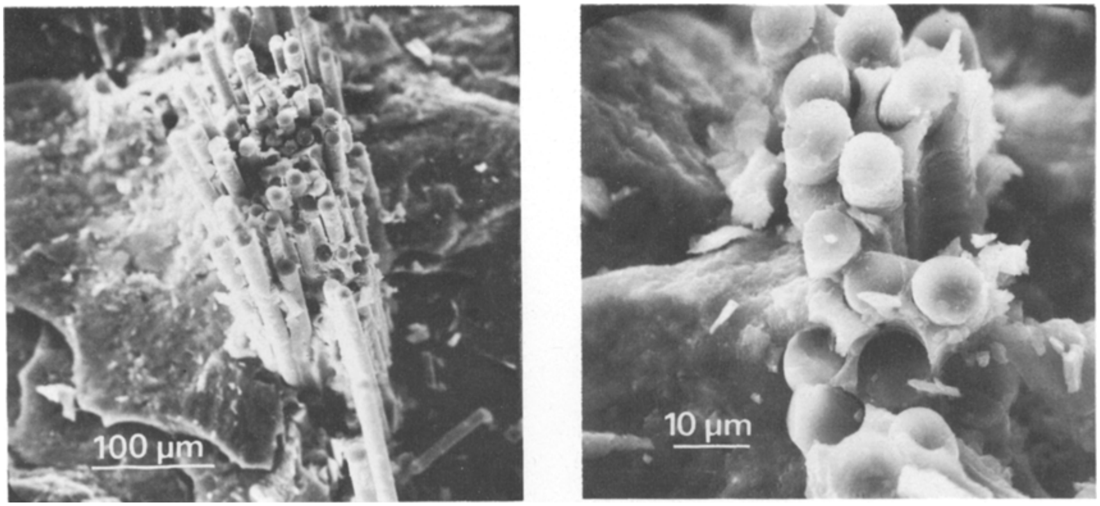

Figure 9 Fracture of fibres near crack surface in 5 year water stored grc.

hydration products have not, at this stage, penetrated into the bundles. This is in marked contrast to the 5 year water stored material (Fig. 9) where all the fibres are completely surrounded by the matrix. Most of the material is crystalline $Ca(OH)_2$.

Some fibres in the "young" grc materials fail prior to pull-out, the number of failures in a particular bundle apparently depending on its shape. The bundles are usually cylindrical in shape as in Fig. 8a, but sometimes they are flattened into tape-like strands (Fig. 8b) during the manufacture of the board.

Nearly all fibre failures which occur, without pull-out, in the young and old grc are at the crack surfaces suggesting that the fibres fail as a result of bending at the crack surface. A few fibres fail beneath the crack surface creating the holes shown in Fig. 10. These fibres, which have not failed at one or the other crack surface, probably failed as a result of the uniaxial tensile stress in the fibres. Premature failures of glass fibres in tension may suggest that the fibres are damaged. Damage to the fibres can occur in two ways, by mechanical abrasion either during manufacture of the fibres or the composite or by alkaline attack after prolonged exposure to wet cement. Since there is a

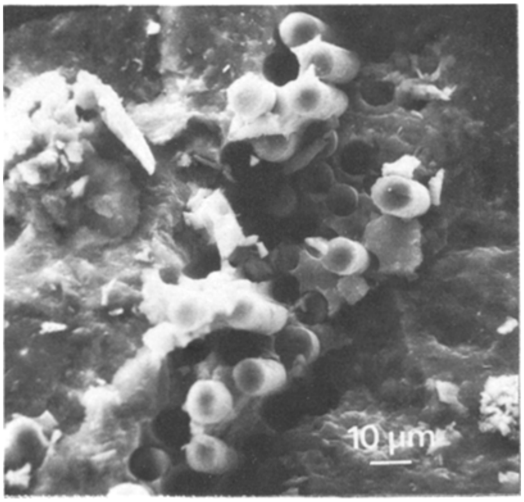

Figure 10 Failure of fibres at the crack surface, due to bending stresses in fibres, and below the surface, due to uniaxial tensile stress in fibres.

greater tendency to a tensile type failure for the fibres in the older material, the latter source of damage is probably more important.

The surfaces of the glass-fibres in 90 day and 5 year wet stored grc are shown in Fig. 11. Some surface degradation has occurred in the fibres from the 5 year material, although the extent of the pitting is not great and the pits are well rounded. Analysis of the fibre-free pull-out grooves in the 5 year water stored grc sample indicate that some ZrO_2 is present in the matrix adjacent to the fibres and extends about 1 μm from the fibre–matrix interface (Fig. 12).

The surfaces of fibres extracted from this 5 year material have been analysed semi-quantitatively and have been compared with analyses on virgin fibres taken from the same batch used to make the board. The results are given in Table II. The results clearly indicate that there is no significant

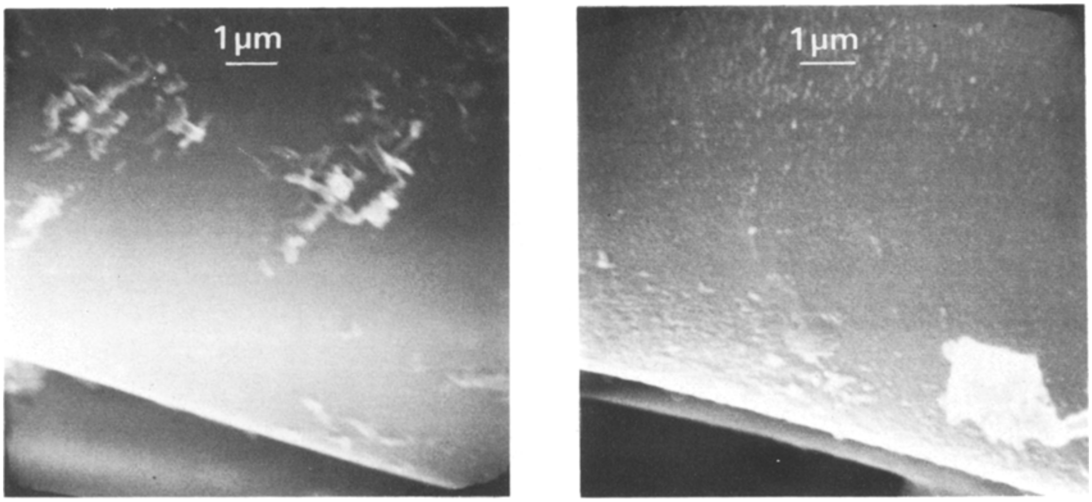

Figure 11 Surfaces of glass fibres extracted from (a) 90 day and (b) 5 year water stored material.

TABLE II Analysis of glass fibres extracted from grc

Fibres	Mean value of % $SiO_2/(SiO_2 + ZrO_2)$	Mean value of % $ZrO_2/(SiO_2 + ZrO_2)$	SiO_2/ZrO_2	95% confidence limit
Virgin fibres washed in acetone	74.9 (10)	24.7 (10)	3.0	0.3
Extracted from 5 year water stored grc;				
(a) Washed in dil. HCl	75.6 (10)	24.0 (10)	3.2	0.4
(b) Unwashed	74.4 (6)	25.2 (6)	3.0	0.2

Numbers in brackets refer to no. of analyses.
$SiO_2/(SiO_2 + ZrO_2)$ and $ZrO_2/(SiO_2 + ZrO_2)$ ratios calculated from calibration curves in Fig. 1.

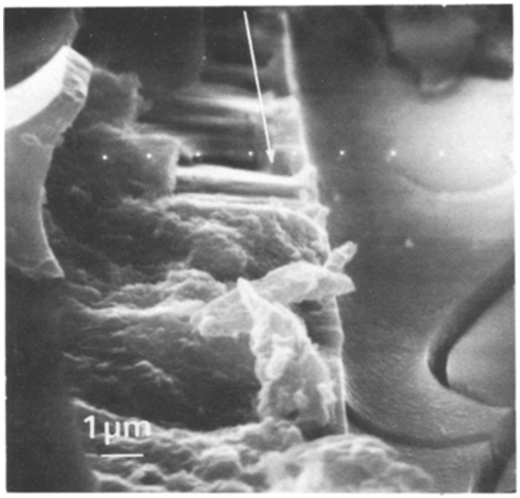

Figure 12 Pull-out groove in 5 year water stored grc showing extent of ZrO_2 rich matrix region. The limit of the region is indicated by the arrow. Spots show positions of the EDAX analyses.

change in the SiO_2/ZrO_2 ratio at the glass fibre surfaces.

3.2. Fibre–matrix interfaces

The previous observations have already shown that the microstructure of the fibre–matrix interface is of paramount importance in the fracture of grc, the reduction of the porosity at the interface and between the fibres in a strand apparently affecting the pull-out of fibres.

The interface can be readily studied in detail using the SEM by "cleaving" grc specimens parallel to the plane of the fibre array. Many fibre-free pull-out grooves are thus revealed for detailed examination.

Fig. 13 shows micrographs of the pull-out grooves in 90 day, dry air (40% r.h.) stored grc. The interface consists of fine fibre-like or whisker-like crystals forming an interpenetrating mat in the voids between partially hydrated cement grains. Morphologically, the whisker-like crystals resemble ettringite, $Ca_6Al_2(OH)_{12}(SO_4)_3 \cdot 26\,H_2O$ or the calcium silicate hydrate CSH(II) [6]. However, an analysis of the crystals using the SEM/EDS system suggests that the molar ratios CaO/Al_2O_3 and CaO/SO_4^{2-} are considerably greater than those to be expected from ettringite and the CaO/SiO_2 ratio obtained in the analysis is also higher than that of CSH(II). It must be borne in mind that X-ray microanalysis of very small crystals is not likely to be very accurate. Diamond *et al.* [7] have shown that the diameter of the area from which X-rays are produced in the SEM is about 1.5 μm. Many of the crystals examined had dimensions smaller than this and, consequently, X-ray emission from the $Ca(OH)_2$-rich matrix could have enhanced the Ca peak intensity. The microanalysis of these crystals is, therefore, thought not to be sufficiently reliable for determining their composition.

With difficulty it was possible to isolate a few whisker-like crystals and examine them by the Debye–Scherrer powder X-ray diffraction method using a camera of 114.6 mm diameter. Even after rather long exposures, only three very faint and diffuse lines were observed on the photographs, occurring at approximately 2.94, 2.80 and 2.00 to 2.10 Å. Obviously, the material was very poorly crystalline, which is uncharacteristic of ettringite,

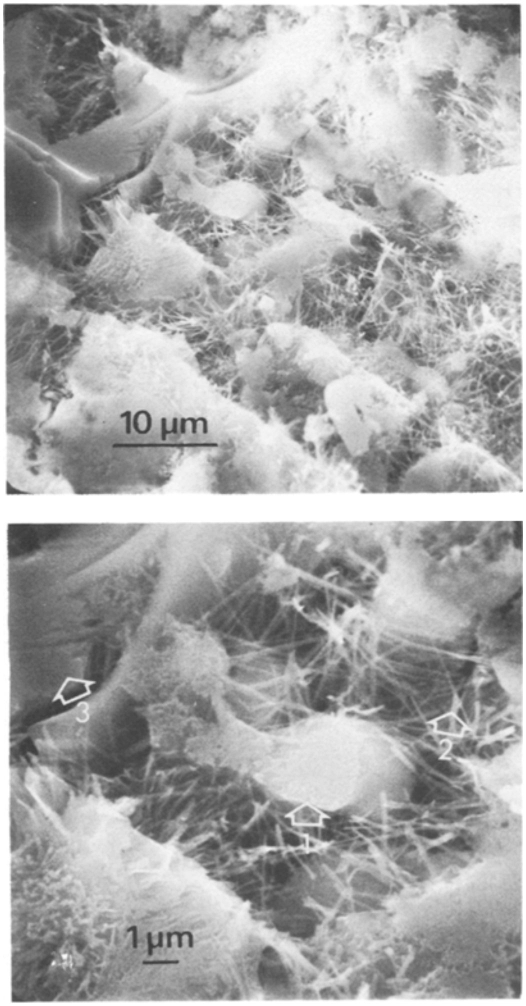

Figure 13 Pull out grooves showing fibre matrix interfaces in 90 day dry air stored grc. (1) Partially hydrated cement grain; (2) "whisker"-like hydration products; (3) $Ca(OH)_2$ crystal.

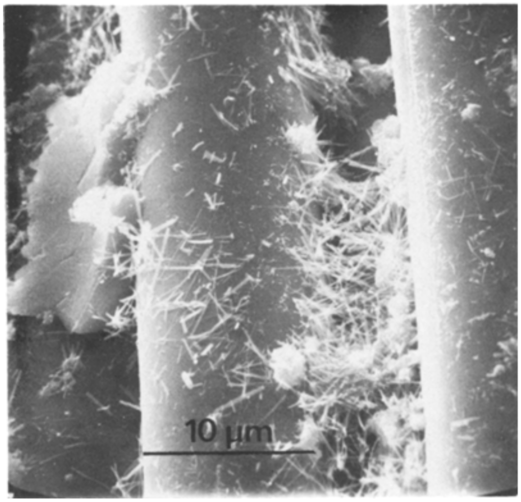

Figure 14 Pulled out glass fibres from 90 day dry air stored material showing good bonding between the "whisker"-like crystals and the fibres.

and the X-ray *d*-spacings also rule out the possibility of the presence of this phase. The X-ray lines could belong to a number of calcium silicate hydrate phases, some of which are known to form with a fibrous habit. The nature of the whisker-like crystals remain uncertain, therefore, pending a more detailed examination CSH(II) is a possibility and it is interesting to note that Gebauer and Harnik [8] have recently published scanning electron micrographs of a fibrous phase in an 84 year old concrete specimen which bear close similarities with those obtained in this study (Fig. 13).

The strength of the interfacial bond will largely depend on the strength of the bond between the whisker-like crystals and the glass fibres. Fig. 14 shows that many of these crystals remain firmly attached to pulled out fibres indicating that the bond strength is at least as good as the strength of the crystals themselves. Clearly, however, the shear strength of the interfaces will be small since the frictional contribution will be low due to the small solid-matrix–fibre contact area.

The interfaces described so far represent those in grc in which the hydration of the matrix has been limited by the dry storage conditions. Fig. 15 illustrates interfaces in 5 year dry air stored grc and it can be seen that they are very similar to those in the 90 day material. If further hydration of the matrix occurs then the density of the matrix increases and the interfaces become almost fully dense (Fig. 16). Most of the material at the inter-

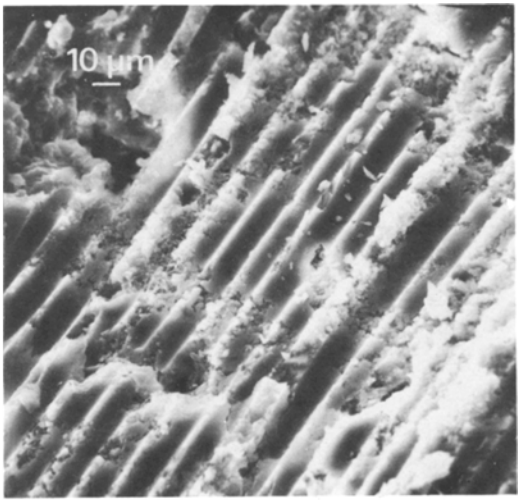

Figure 15 Fibre–matrix interfaces in 5 year air stored grc.

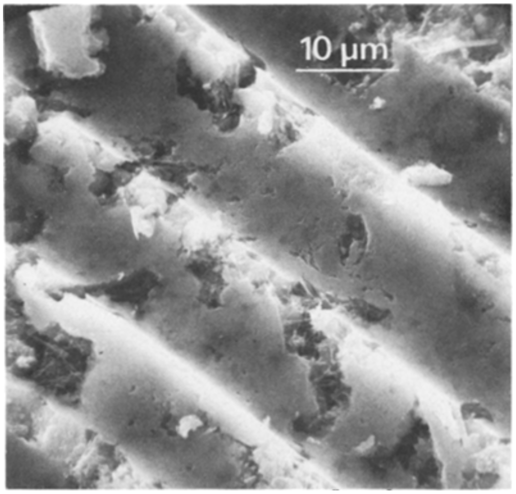

Figure 16 Fibre–matrix interfaces in 90 day moist air stored grc.

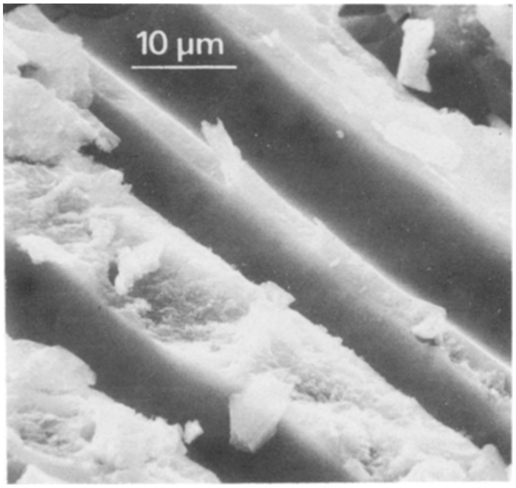

Figure 17 Fibre–matrix interfaces in 5 year water stored grc.

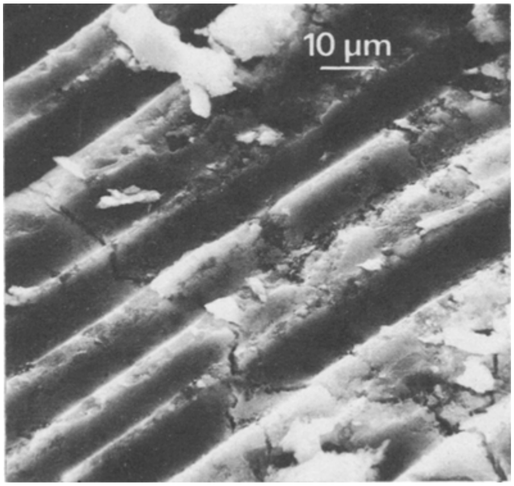

Figure 18 Fibre–matrix interfaces in 5 year naturally weathered grc.

face is $Ca(OH)_2$, and some of the whisker-like crystals are observed in the residual porosity. The void/solid contact area ratio, as found by point counting on several micrographs, decreases from about 1.7 in the 40% r.h. air stored grc to 0.2 at 90% r.h. The residual porosity in the 5 year water stored material is almost nil (Fig. 17), and the interface can be considered as totally solid contact between the $Ca(OH)_2$ of the matrix and the fibres.

Although the bond strength between the $Ca(OH)_2$ crystals and the glass fibres is relatively small, little or no matrix is observed adhering to pulled out fibres; the frictional component of the interface shear strength will be increased considerably due to the larger solid-matrix–fibre contact area.

The microstructure of the interface in the 5 year naturally weathered material vary from the porous type observed in dry storage to the fully dense of the wet stored material (Fig. 18). The different types of interface being observed in different parts of the sample. The reasons for this are not clear but it may be due to the variation in hydration conditions in different parts of the composite resulting from changes in atmospheric humidity and temperature experienced during natural weathering.

4. Discussion

The results presented in the previous sections have shown that the mode of failure of grc is dependent on its age and conditions of storage. The most significant microstructural changes occur in the matrix during the hydration of the cement resulting in the modification of the fibre–matrix interface regions. It will, therefore, be necessary to discuss these changes in relation to the stresses developed in the fibres and the matrix during fracture and to the propagation of cracks in the matrix.

The experimental evidence suggests that glass fibre failures occur when the bending stresses in the fibres at the surface of a transverse crack exceed a certain stress value. This stress, σ_f, will be given by the Griffith relation,

$$\sigma_f = \left(\frac{2\gamma E}{\pi C}\right)^{1/2} \qquad (1)$$

where γ is the surface energy of fracture of the glass fibre, E is its Young's modulus and C is the length of a surface flaw. In "virgin" glass fibres $\sigma_f \simeq 1.8\,\text{GN m}^{-2}$, $\gamma \simeq 5\,\text{J m}^{-2}$ and $E \simeq 70\,\text{GN m}^{-2}$, giving a value of the flaw size of $0.06\,\mu\text{m}$.

The micrographs of the surfaces of corroded glass fibres show that the flaw size is considerably larger than this. Previous investigations [5] have shown that the tensile strength of corroded fibres decreases to about $1.1\,\text{GN m}^{-2}$ after about 200 days exposure to a Portland cement extract solution, and thereafter their strength remains roughly constant. This implies that the flaw size is about $0.15\,\mu\text{m}$, and indeed flaws of this order of matnitude can be observed on the surfaces of the corroded fibres (Fig. 11). The weakening of the fibres will not, however, drastically alter the toughness of the composite but will result in a reduction of the ultimate strength.

Fig. 19 shows schemmatically how a fibre, oriented at an angle θ with respect to the applied tensile stress, is bent when a transverse crack is opened by a displacement, ϵ_c. A considerable bending strain will be experienced by the fibre where it emerges from the crack face at X and X′. Accordingly, stresses will also be produced in the matrix. The stress at the surface of the fibre will depend on the radius of curvature, R, at these points. Using simple bending theory and assuming the uniaxial tensile stress on the fibres is small compared to the bending stresses, the stress in the fibre on its outer surface σ_B is,

$$\sigma_B = \frac{Er}{(R+r)} \qquad (2)$$

where r is the radius of the fibre cross-section. Assuming that $\sin\theta/2 \simeq l/2R$, where l is the length

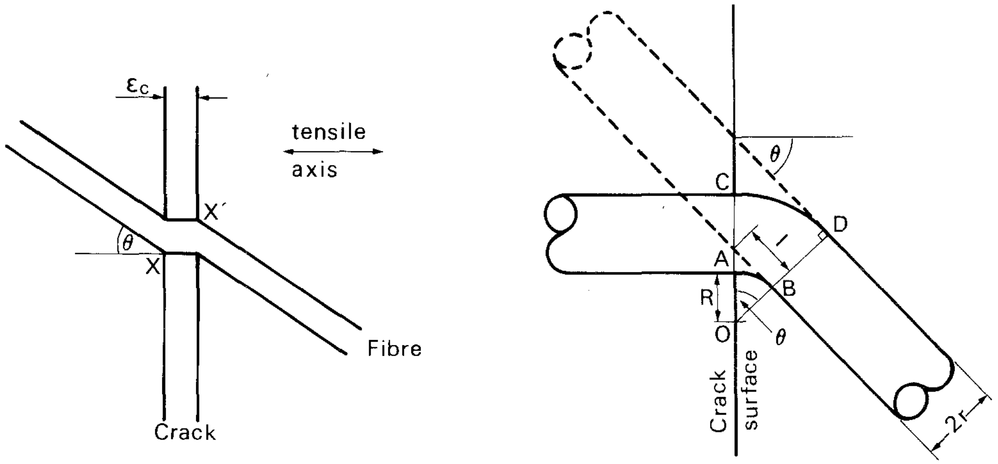

Figure 19 Schematic representation of the bending of fibres bridging a transverse crack during fracture.

of the bent region of fibre, then,

$$\sigma_B \simeq \frac{2Er\sin\theta/2}{l + 2r\sin\theta/2}. \qquad (3)$$

Substituting appropriate values of $\sigma_B \simeq \sigma_f \simeq 1.8\,\mathrm{GN\,m^{-2}}$, for uncorroded fibres, and $r = 5\,\mu\mathrm{m}$; then for bending to occur without failure, $l \geqslant 200\,\mu\mathrm{m}$ for all values of θ from 0 to 90°. Thus we can see that for all fibres to remain unbroken during fracture, and assuming they are undamaged by corrosion, the value of l or the radius of curvature of the bent fibres is large. It is, therefore, possible to relate most fibre failures in grc to certain microstructural features which will limit l to less than $200\,\mu\mathrm{m}$.

Generally, l is observed to be greater than $200\,\mu\mathrm{m}$ in the 90 day old materials due to three possible microstructural features: (i) the presence of wide cracks around the fibre bundles resulting from the delamination of the composite, (ii) the crumbling of the matrix around the bundles, probably due to the stresses imposed on the matrix by the bent fibres, and (iii) the absence of hydration products between the fibres within the strands. On the other hand, the absence of these features in the older water stored and naturally weathered grc typically limits l to a few microns. Fig. 20 shows several fibres which have failed at the crack surface, and at the point of emergence from the matrix the radius of curvature is very small. The fracture initiation sites in the glass fibres can also be seen, which are, as expected, on the outer surfaces of the fibres at the position of maximum strain.

Other workers such as Morton and Groves [9], Aveston [10] and Aveston *et al.* [11] have also observed the effects of bending misaligned fibres at crack faces in fibre-reinforced cement and other brittle matrix composites.

The fibre–matrix interface in any composite material is important since it can affect the transfer of stress from the matrix to the fibres and the propagation of cracks in the matrix in the vicinity of the fibres. The interface in the dry air stored materials will be inherently weak due to the small contact area between the matrix and the fibres. However, they will be very compliant due to the numerous separate bonds between the fibres and the whisker-like crystals and the high porosity. The failure of such an interface will tend to be gradual

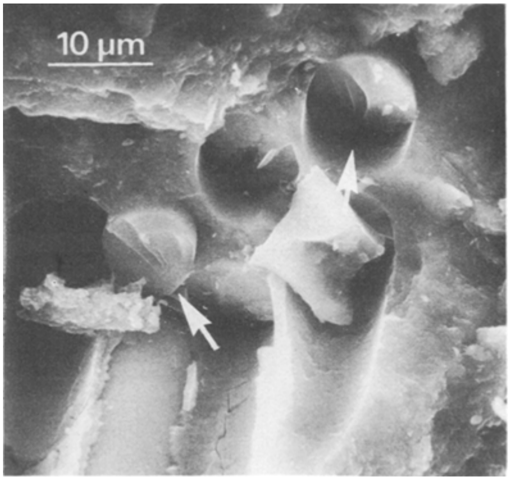

Figure 20 Fracture initiation sites (indicated by arrows) in glass fibres bent at fracture surface in an upward direction.

with progressive failure of the individual bonded crystals and, therefore, should contribute significantly to the toughness of the composite as a whole.

Furthermore, this type of porous interface could provide an effective barrier to the propagation of cracks. The stress concentration at the tip of a crack approaching the fibres will be relaxed at the interface, since the porous and compliant interface region will be able to accommodate much of the strain at the crack tip. This will then slow down the moving crack around the fibre strand, and if the strands are close enough together the entire length of the crack front may be halted, at least temporarily. This will necessitate the propagation of subsidiary cracks in the matrix to accommodate further applied strain. The formation of the subsidiary crack structure in dry stored grc, resulting in a large fracture surface area, gives rise to the high energy failures associated with the observed values of toughness, "ductility" and impact strength.

The dense type of interface present in the water stored grc will be much less compliant than the porous types, although the shear strength will be higher due to the increased frictional component. These interfaces will be less able to relax the stress concentrations at the crack tip and thus the primary crack will be able to propagate relatively freely around the fibre bundles until, ultimately, complete failure of the matrix occurs. The stress on the composite will then be supported by the fibres alone. Thus the failure surface area will be small, approximately equal to the cross-sectional area of the test specimen, and accordingly by the toughness will be relatively low.

This work indicates that both the microstructure of the matrix and the properties of the fibre reinforcement, play important roles in determining the mechanical properties of grc composites. It is difficult, at this stage, to quantify the relative contributions of fibre and matrix, and both areas offer scope for further research.

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