JOURNAL OF MATERIALS SCIENCE 20 (1985) 3610–3620

The microstructure of the steel fibre–cement interface

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The microstructure of the steel fibre–cement paste interface was studied by scanning electron microscopy. The interfacial zone surrounding the fibre was found to be substantially different from the "bulk" paste further away from the fibre surface. The interfacial zone consisted of (a) a thin (1 or 2 μm thick) duplex film in actual contact with the reinforcement, (b) outside of this, a zone of perhaps 10 to 30 μm thickness, which, in reasonably well hydrated systems, is largely occupied by relatively massive calcium hydroxide crystals, with occasional interruptions of more porous regions, and (c) outside of this, a highly porous layer parallel to the interface. The interaction of cracks initiated in the matrix with this interfacial zone was observed.

1. Introduction

The properties of composite materials are very sensitive to the structure of the interface between the reinforcing inclusion and the matrix. It is now well established that in composites with portland cement matrices (mortars, concretes, fibre-reinforced cements) the structure of the paste near the interface is significantly different from that of the bulk paste. Early work [1–4] has indicated that the interfacial zones around aggregate particles and fibres embedded in cement paste matrices are rich in CH†; Bache *et al.* [2] reported that a layer of CH as thick as 50 μm can form around the aggregate particles.

Detailed studies of the cement–aggregate interfaces carried out at Purdue University [5–8] have revealed a complex structure consisting of two elements: a thin duplex film layer of about 1 μm thickness immediately adjacent to the aggregate surface, backed up by a thicker interfacial zone of paste different in structure and more porous than the bulk cement paste. The thin duplex film itself consisted of two layers: a continuous crystalline film of CH deposited on the aggregate surface with, presumably, the *c*-axis perpendicular to the surface, and a second thin layer of C–S–H gel, one particle thick. The interfacial zone was estimated to be perhaps 50 to 100 μm thick, and it ordinarily contained clusters of C–S–H gel, some ettringite, and large CH crystals of various orientations. The zone is ordinarily much more porous than bulk cement paste, and is often characterized by the presence of hollow shell hydrated grains (Hadley grains). In some cases a portion of the extra space adjacent to the duplex film was partially filled with thin, small CH platelets stacked face to face (secondary CH). The observations were made in experimental studies in which separation along the aggregate–cement paste interface was obtained by shrinkage induced cracking, and the exposed surfaces (paste side and aggregate side) were observed by scanning electron microscopy (SEM).

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†Cement chemistry notation is used: C = CaO, S = SiO_2, A = Al_2O_3, F = Fe_2O_3, $\bar{S}$ = SO_3, H = H_2O.

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Charles-Gibergues *et al.* [9] found by X-ray diffraction, that the CH close to the interface was always highly oriented. The degree of orientation was usually found to decrease with distance from the interface, becoming essentially random at a distance which varies with the system but typically is around 50 μm. These authors define the thickness of the interfacial zone as the distance inward of the interface within which CH can be demonstrated to show preferred orientation.

The structure of the steel–cement paste interface was investigated by Al-Khalaf and Page [10] using cylindrical specimens, the bottom half of which was made of steel and the upper half of cement paste. These specimens were broken in uniaxial tension, and it was found that the fracture occurred in the paste very close to the interface for young specimens, and at the interface for older specimens. The exposed surfaces were studied by SEM. A similar study was carried out by Pinchin and Tabor [11] using cylindrical paste specimens with a single steel fibre embedded in the centre. The specimens were split to expose the interface and the tensile fracture faces of the steel and cement paste were observed with SEM.

Al Khalaf and Page [10] reported that the paste side of the interface consisted of a discontinuous CH layer (< 1 μm thick) that replicated the topography of the steel surface, with the *c*-axis oriented normal to the steel surface. The CH exhibited a dendritic growth and in many cases crystal boundaries could be observed. In addition to this layer, there was frequent evidence of a C–S–H gel of various morphologies, and well developed crystals formed at different orientations. The C–S–H gel was not densely packed near the interface. It occasionally could be observed adhering to the steel surface, but usually it was confined to the paste side of the interface. Pinchin and Tabor [11] also reported observing cement paste interfaces rich in CH. However, they did not observe a film-like layer, but rather a structure consisting of a smooth surface of CH and porous material made up of C–S–H and some ettringite. Pinchin and Tabor [11] did not discuss the orientation of the CH at the interface and it is difficult to resolve from their micrographs whether it tends to form a film, as observed by Hadley [5], Barnes *et al.* [6–8] Al-Khalaf and Page [10].

A detailed study of the cement paste–glass interfaces in glass fibre reinforced cement (GRC) was reported by Stucke and Majumdar [12]. In air-stored specimens there was little deposition of hydration products between the individual filaments in a strand, but on prolonged water curing the spaces between the filaments were densely filled with CH. From other studies [13, 14] involving GRC systems it appears that the CH tends to be oriented with its *c*-axis parallel with the filament axis. Stucke and Majumdar [12] did not report observations of a duplex film on the glass surface itself but Cohen and Diamond [15] presented micrographs in which such a film could clearly be seen. The presence of massive CH around glass filaments was also reported by Jaras and Litherland [16].

In recent studies [17, 18] in which a load crack was induced in cement paste specimens, and forced to propagate past steel fibres embedded perpendicular to the crack path, SEM observations indicated that in many cases the propagating crack did not actually intersect the fibre, but rather its progress was arrested 20 to 50 μm in front of the fibre. At that point its path orientation was changed by about 90° and it continued as a crack running parallel to the fibre, at distances of 20 to 50 μm from the fibre interface itself. Illustrations of this behaviour are shown in Figs. 1a and b. In other experiments, where the specimens were dried before loading and the matrix did not exhibit shrinkage cracking, debonding of the interface itself was seen to take place (Fig. 2).

Cracking patterns such as the ones shown in Figs. 1a and b can be the result of a crack arrest mechanism involving a weak interface [19]. However, in order to apply such an explanation the structure of the interfacial zone at a distance of 50 μm from the fibre surface should be characterized. Some of the studies reviewed previously suggest the presence of porous weak zones at such distances, with some of the pores filled with CH. However, these conclusions were based on observations of the surface of the paste side of the interface, within a few μm of the fibre surface. In the present case, the zone of interest was 20 to 50 μm from the fibre surface and so it was felt that additional study was required. The object of the present work was to study the structure of the paste in the vicinity of the fibre, which is revealed when the specimen is fractured perpendicular to the fibre axis. At the same time,

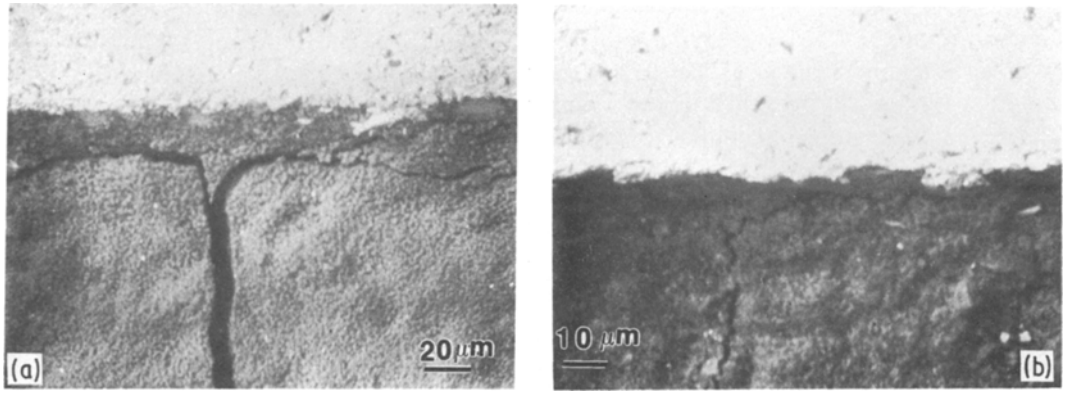


Figure 1 Interactions of cracks initiated in the matrix with steel fibre reinforcement, showing crack arrest and "pseudo debonding" in the matrix. (a) Load induced crack, (b) shrinkage induced crack. The crack propagates in the upward direction. The bright part of the micrograph is the steel fibre.

the microstructure of the surface exposed when the fibre was removed was also studied.

2. Experimental details

2.1. Materials

The cement pastes were made from an ASTM Type I portland cement and at a water : cement ratio of 0.35.

The steel fibres used were straight portions of Dramix ZC 60/50 fibres produced by Bekaert Co. (Belgium). They had a circular cross-section of 0.5 mm diameter. They were initially treated with acetone and trichloroethane to remove the polymer coating and clean the surface.

2.2. Observations in the SEM

All of the observations were carried out in an SEM (ISI Super III-a) equipped with an energy dispersive X-ray analyser (EDXA-EG & G Ortec, EEDs II). The specimens were oven dried and sputter coated with a 30 nm layer of gold palladium.

2.3. Specimens

The specimens were similar to those tested for crack propagation in previous work [17, 18, 20]. They consisted of notched cement paste compact tension specimens in which a steel fibre was placed at the upper face in front of the notch and perpendicular to it (Fig. 3). The specimens were prepared in a special mould in which the fibre was placed at about 0.3 mm above the bottom and the paste was cast around and above it. After curing for 4 to 6 weeks in lime water the surface closer to the fibre (the original bottom face of the mould) was ground and polished to expose the fibre to a depth of approximately one half of the fibre diameter. Later on, this face was

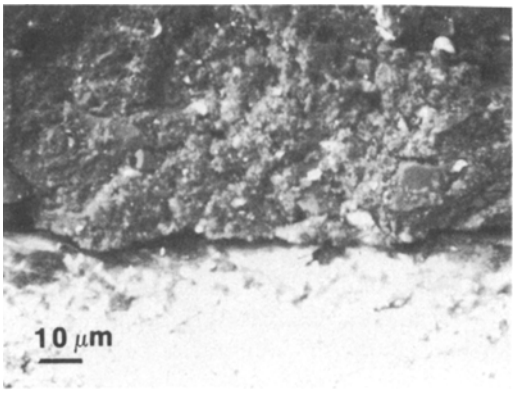


Figure 2 Shrinkage induced crack at the actual steel fibre–cement interface. The bright part of the micrograph is the steel fibre.

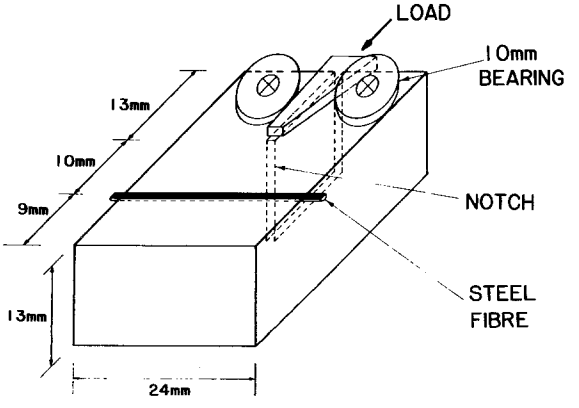
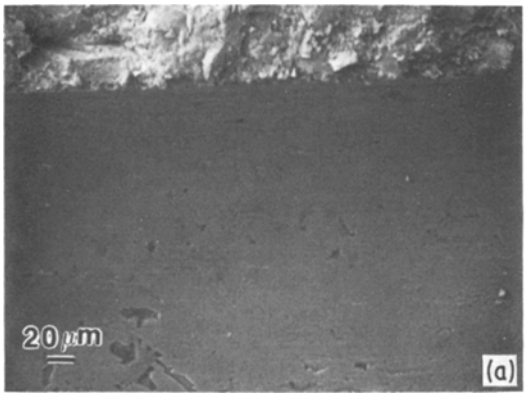
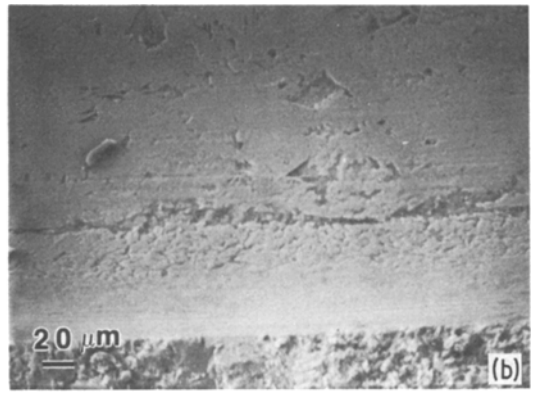


Figure 3 Description of a compact tension specimen reinforced with a steel fibre.





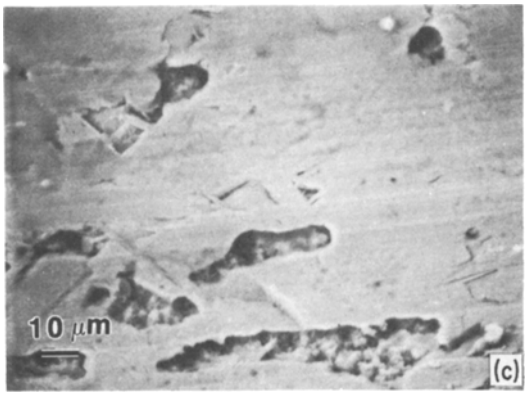


Figure 4 The surface of a groove underneath a steel fibre showing (a) a zone of smooth surface with hardly any defects, (b) a zone of smooth surface with some defects, and (c) higher magnification of such defects.

kept upwards for observations in the SEM. The fibres protruded from the sides of the specimen so they could be easily peeled off by applying a small upward force to expose the interface.

Four series of tests were carried out in the present work:

Series I: uncracked specimens. The fibre was peeled off the saturated surface dry (SSD) specimen, and the exposed groove was observed.

Series II: cracked specimens. SSD specimens were wedge loaded until the first crack was observed. The fibre was peeled off and the groove surface observed.

Series III: fractured specimens. The fibre was peeled off the SSD specimen which was then wedge loaded until it fractured into two halves. The surface of the groove and the fracture surface perpendicular to the groove were observed.

Series IV: The surfaces of fibres peeled from the paste and companion fibres that were not cast in paste were observed.

3. Observations

3.1. Series I: uncracked specimens

The surface of the groove consisted of a very smooth and continuous layer, with some local defects (Fig. 4), but no cracks.

3.2. Series II: cracked specimens

In the vicinity of the cracks the smooth layer reported in series I seemed to have been broken (Fig. 5), exposing beneath it an open and porous structure (Fig. 6). The thickness of the layer can be estimated, from observations of broken fragments (Fig. 7), to be less than 1 μm. This layer, which is rich in CH, corresponded to the duplex film described by Barnes *et al.* [6–8]. The exposed surface underneath this film (Figs. 6 to 8) shows the presence of CH crystals, some of them quite massive (upper part of Fig. 8a) and some of them less than 1 μm thick (Fig. 8b), with their c-axes parallel to the plane of the interface.

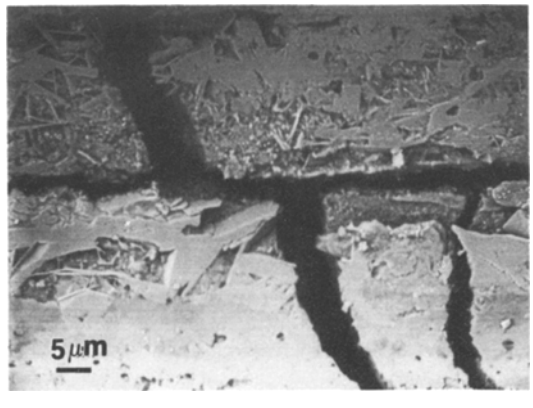


Figure 5 The surface of a groove underneath a steel fibre at the zone where a crack propagated around the fibre, showing a rough surface in the vicinity of the crack.

Figure 6 Higher magnification of the surface of the groove adjacent to a crack that propagated around a steel fibre.

These micrographs also indicate the presence of agglomerates of particles which are less than 1 μm diameter, presumably C–S–H and rod shaped fibrous particles greater than 1 μm long with diameter less than 0.1 μm. Because of their small size it was not possible to resolve the compositon of such fibrous particles by EDXA, but there are indications that at least some of them could be ettringite.

3.3. Series III: fractured specimens

Observations of the fractured plane perpendicular to the fibre–cement interface revealed the changes in the structure of the paste side of the interface, extending from zones close to the interface to regions which are deeper in the paste.

In more than 50% of the cases, a rim of massive material, presumably CH (C/S > 10), with a thickness of 5 to 15 μm, could be clearly seen (Fig. 9). In some instances the material in the rim was so massive that it was difficult to resolve the orientation of the crystals (Fig. 10a), but in other locations CH platelets could be observed, with the *c*-axis parallel to the plane of the interface (Fig. 10b). In some cases there were clear indications that the CH rim was not in direct contact with the steel surface and a thin layer (~ 1 μm) of hydration products could be observed (upper right-hand side of Fig. 10b).

The CH rim was not continuous, and porous zones could be observed alongside the massive CH crystal (Figs. 11a and b). In many cases the porous structure consisted of fibrous material (Fig. 11d), some of it tending to grow between CH crystals (centre of Fig. 11b). Owing to the small cross-section of these fibrous particles it was difficult to resolve with certainty their composition, but they were rich in aluminium and sulphur, suggesting that at least some of them were ettringite. Formation of ettringite in open spaces around interfaces was reported by other investigators [5, 6, 11]. The micrographs in Fig. 11 indicate that CH crystals with different orientations could be formed in neighbouring regions (Figs. 11b and c) but in all cases their *c*-axis was parallel to the plane of the interface.

It is interesting to note that the area backing the CH rim tended in many cases to be very porous (Figs. 10 and 12). A transition zone could be observed, which was very porous at the CH surface and became denser as the bulk paste was approached (Fig. 12). This transition zone was about 10 to 20 μm thick, and beyond it the usual features of a dense structure with

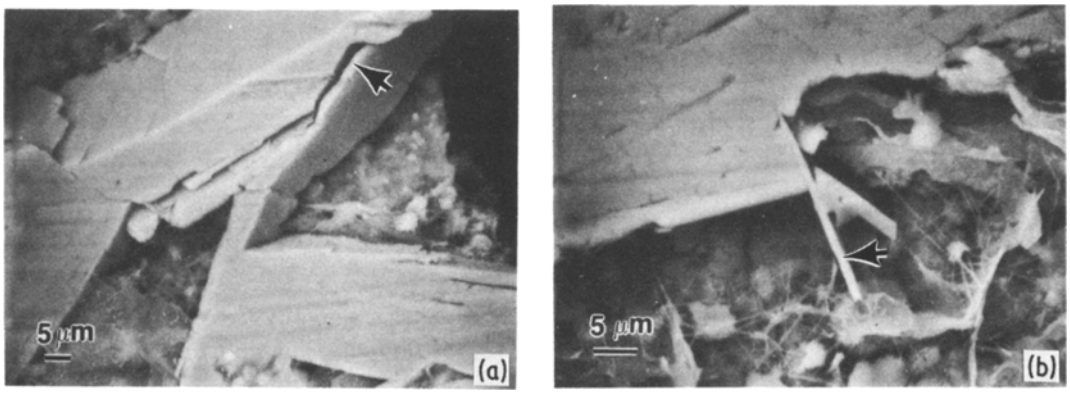


Figure 7 The surface of the groove adjacent to a crack that propagated around a steel fibre showing a broken film layer (marked by arrows) and the porous material which is exposed underneath it.

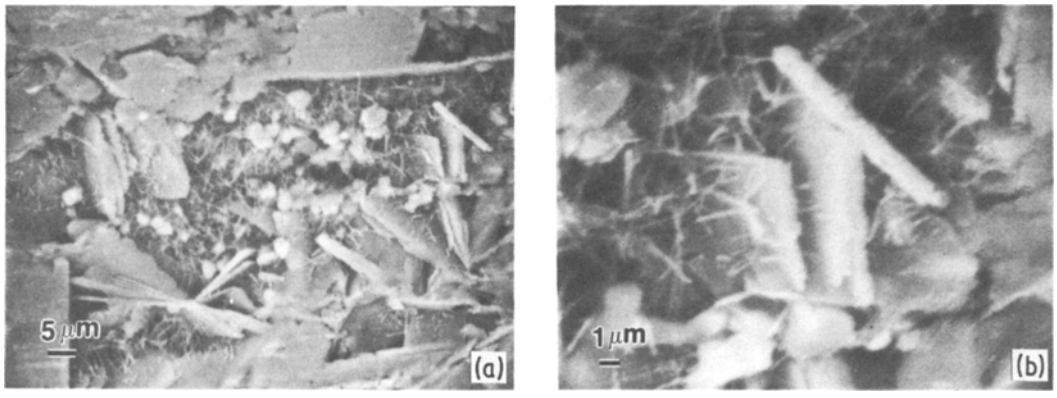


Figure 8 Exposed surface underneath the duplex film, showing crystalline CH and porous material.

unresolvable feature (typical to well hydrated 0.35 w/c ratio pastes), can be seen.

In some regions there was no presence of a massive CH rim, but rather a porous structure consisting mainly of C–S–H (Figs. 13a, b and c) with some individual crystals of CH, that can be more clearly observed in Fig. 13d. It is interesting to note, in Figs. 13a and b, the presence of a $\sim 0.5\ \mu m$ layer at the interface. This is probably the duplex film that could be seen in the first two series of experiments, but was seldom observed in this series of tests.

Typical micrographs of the groove surface of Series III specimens are shown in Figs. 14a and b. Most of the area is occupied by massive CH, engulfing zones of porous material consisting mainly of C–S–H (Fig. 14c) and sometimes ettringite. The CH is oriented with the *c*-axis parallel to the plane of the interface and within this plane it can assume different orientations. In most cases no duplex film could be observed as was the case in the first two series of experiments. There are indications that the duplex film was broken during preparation of the specimens in this series and therefore the micrographs in Figs. 14a, b and c are representative of the structure underneath this film. In a few cases the remnants of a calcium rich film could be observed (left side of Fig. 14d). The crystals sometimes show a hexagonal habit, with the *c*-axis roughly perpendicular to the surface and a thickness of less than 1 μm.

3.4. Series IV: fibre surface

A typical surface of a fibre before it was cast in a cement matrix is shown in Fig. 15a. The surface is generally smooth, but frequently defects which are oriented along the fibre axis can be observed. After removal from the paste, most of the fibre surface seemed to be free from any deposit of hydration products, and only occasional local "pockets" of adhering paste

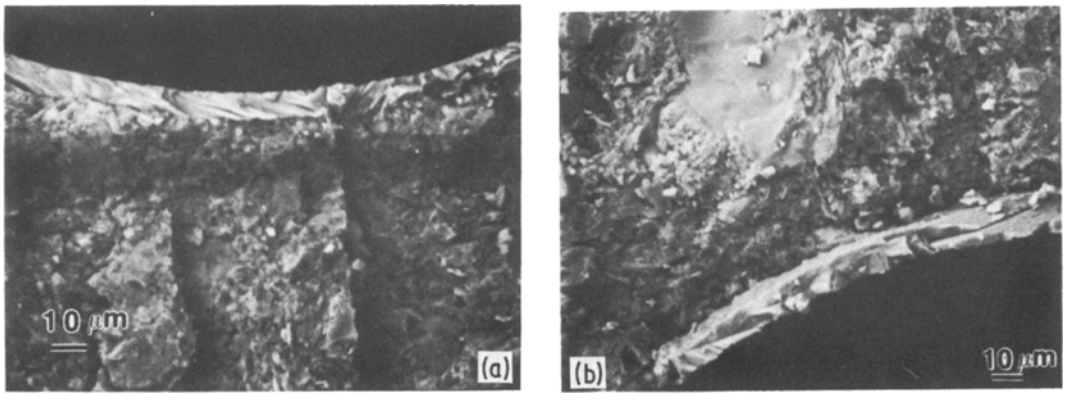


Figure 9 A rim of massive CH observed around the fibres on surface fractured perpendicular to the fibre axis.

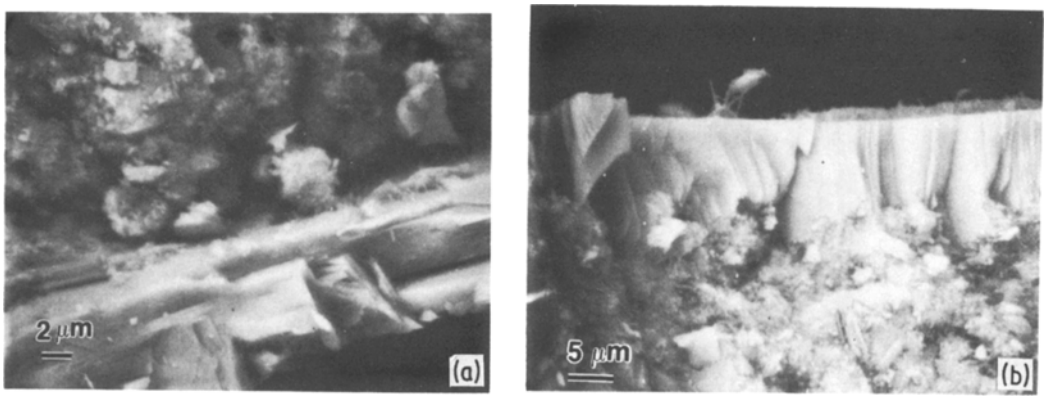


Figure 10 Higher magnification of the CH rim.

could be observed (Fig. 15b) which consisted of plate-like crystals and fibrous and particulate material (Fig. 15c).

3.5. Cracks

In some of the specimens tested in the Series III, cracks could be observed, running from the bulk cement paste toward the interface. It is difficult to tell whether the cracks are the result of loading stresses or whether they were induced by drying during the preparation of the specimens for SEM observations. The interaction of the

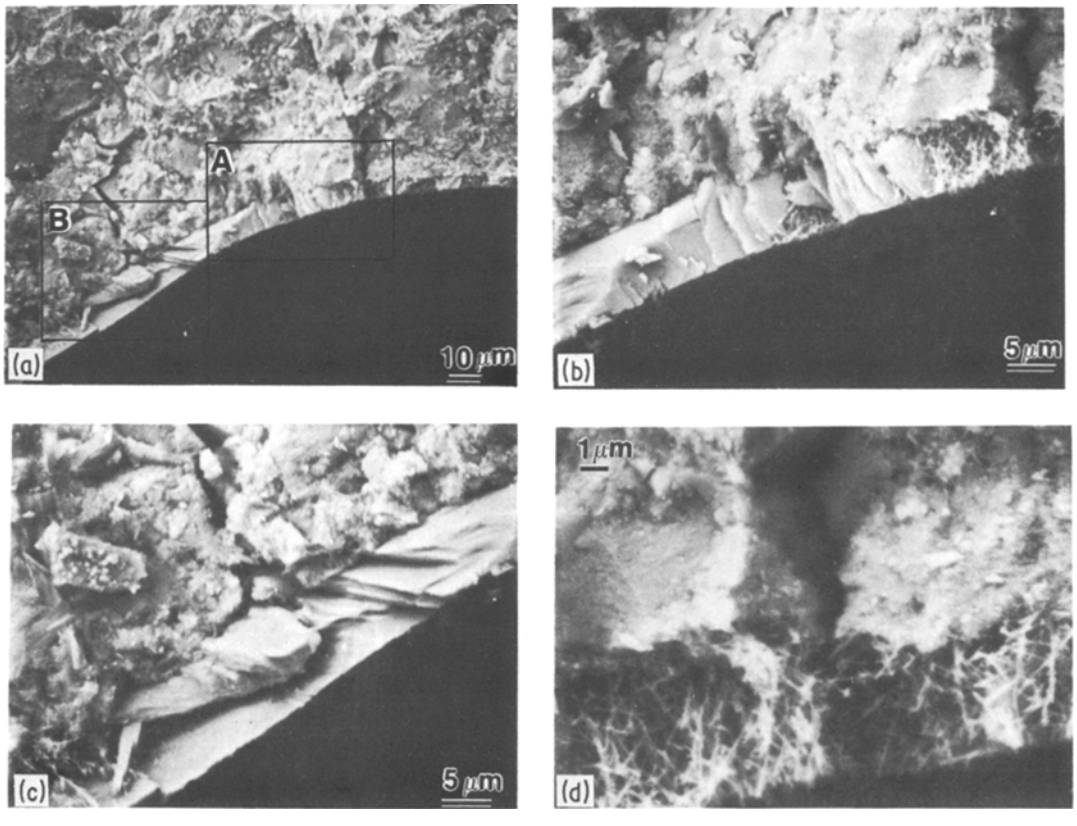


Figure 11 A zone of the CH rim showing discontinuities and cracking. (a) General appearance of the zone. (b) Higher magnification of the centre of the rim showing pockets of porous material [higher magnification of field A of (a)]. (c) A crack arrested and deviated at the CH rim, which prevented it from advancing toward the fibre [higher magnification of field B of (a)]. (d) A crack running through a porous pocket in the CH rim [higher magnification of the field around the crack at the right side of (b)].

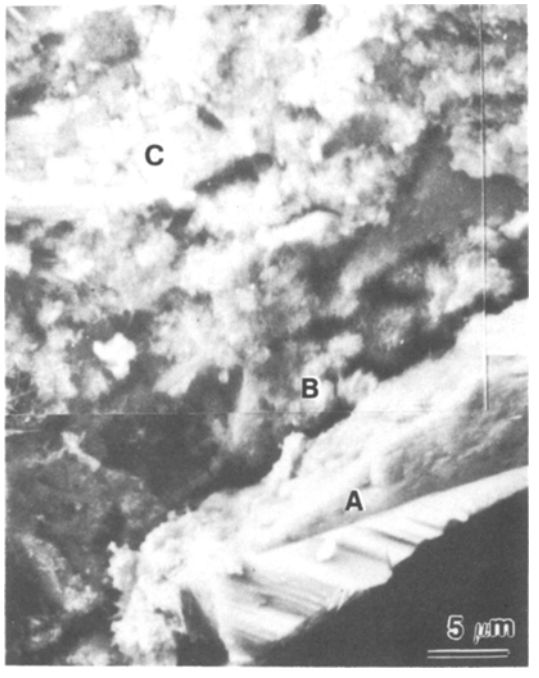


Figure 12 Interfacial zone exposed on fracturing perpendicular to the fibre axis showing the rim of CH layer (A), a porous layer backing this rim (B) and the dense, bulk cement paste (C).

crack with the zone around the interface is of interest, since it would be expected that, regardless of the mechanism by which it was initiated, the propagating crack would tend to follow the path of least resistance, i.e. a path through the weaker zones around the interface.

Several cracks could be observed in some of the micrographs shown previously (Figs. 11a, c and d; Fig. 13b) and in additional micrographs, Figs. 16 and 17. From these pictures two types of crack interactions with the zone around the interface can be seen: in one type, the cracks approaching the CH rim (Figs. 11c, 16 and 17) tend to be arrested and their direction shifted by about 90°, so that they subsequently travelled parallel to the rim at a distance of about 10 μm from the interface. The structure in this region was shown to be quite porous (Fig. 12) and the crack would presumably prefer to deviate toward it rather than continue straight through the massive CH layer. In the other type of intersection, cracks approaching a porous zone where no massive CH rim exists do not show any tendency to deviate, and seem to continue

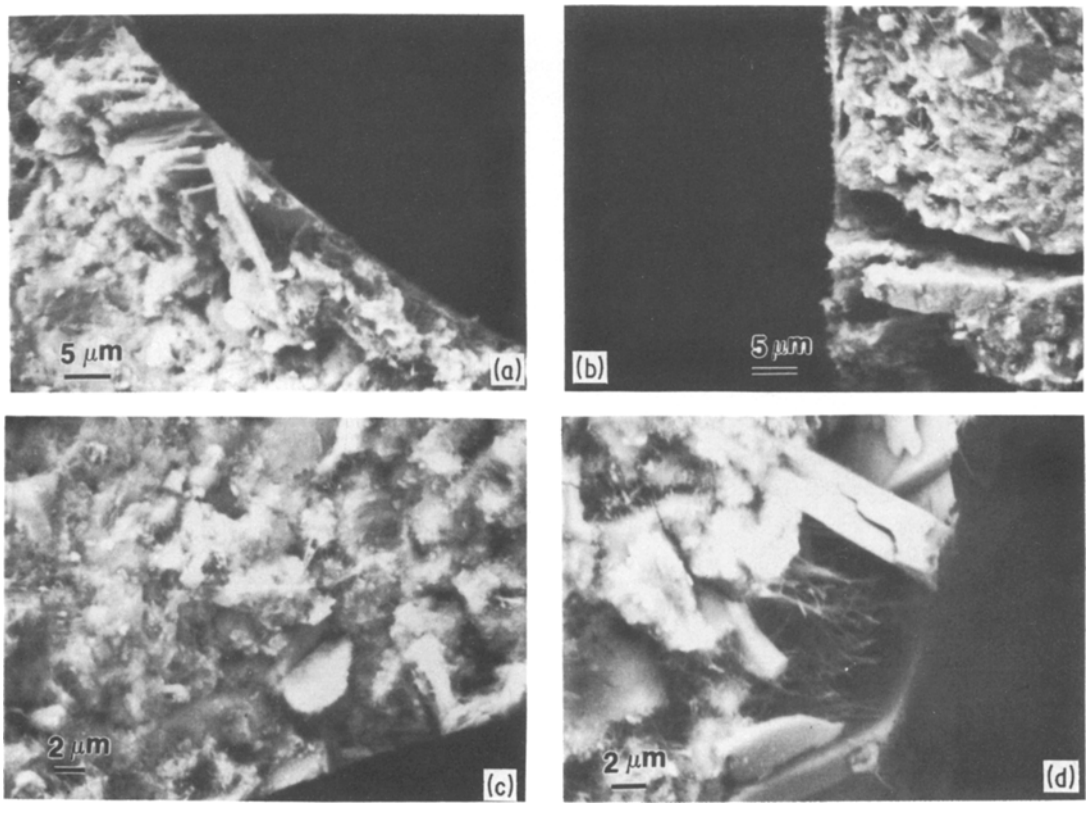


Figure 13 Zone around the fibre–cement interface exposed by fracturing perpendicular to the fibre axis where no rim of CH could be observed.

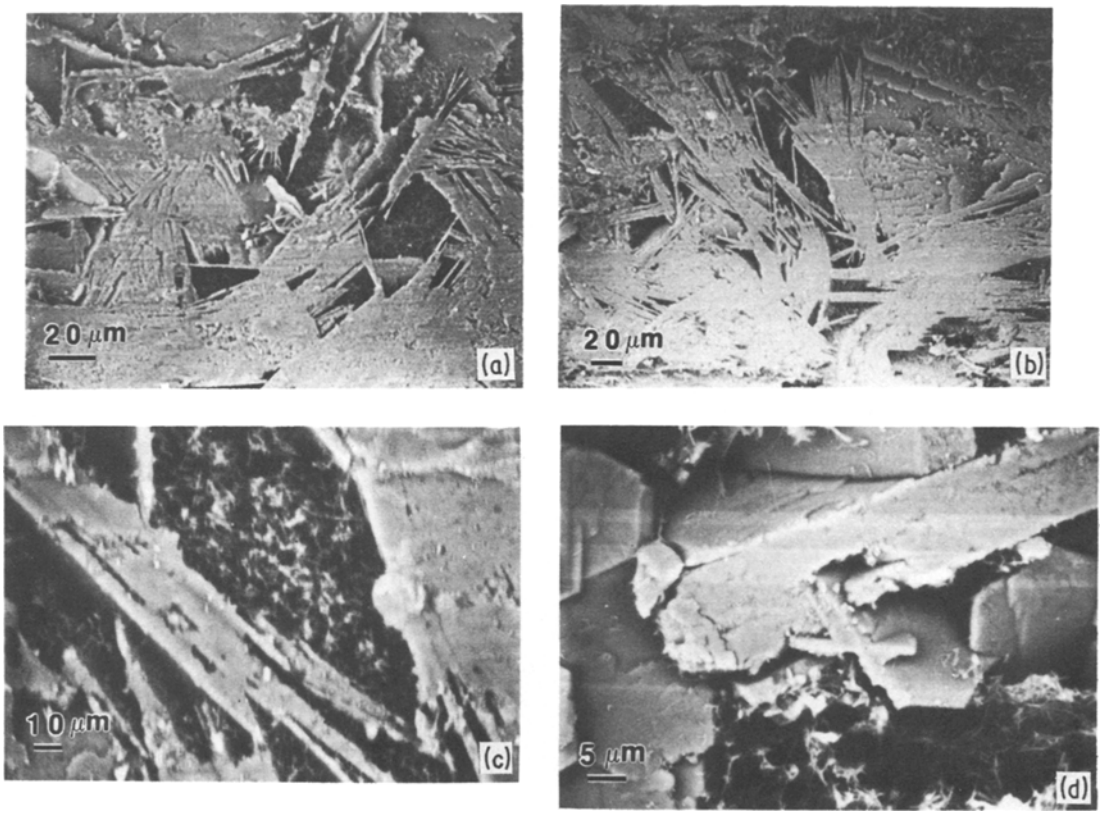


Figure 14 The surface of the groove showing massive CH engulfing pockets of porous material (a), (b), (c) and thin plate-like material, which is a remnant of the duplex film that was probably broken during the removal of the fibre (d).

straight ahead to the interface, at the duplex film (Fig. 13b).

4. Discussion and conclusions

The results of the present study indicate that the general characteristics of the steel–cement paste interface are similar to those described by Hadley [5] and Barnes *et al.* [6–8] for pastes in contact with mineral aggregate or glass. There is a thin duplex film ($< 1\,\mu m$) in direct contact with the steel, backed by an interfacial zone. However, in the present case there are clear indications that a major component of the interfacial zone is a rim of massive CH, approximately $10\,\mu m$ thick backed up by a transition zone (10 to $20\,\mu m$ thick) which is very porous adjacent to the massive CH rim and gradually becomes denser as it approaches the bulk cement paste matrix. The interfacial zone also includes regions where no CH is deposited, but which contain rather a porous mass of C–S–H, ettringite, and individual CH crystals in contact with the duplex film. Hadley [5] and Barnes *et al.* [6–8] did not report the occurrence of massive CH to such an extent, although it was visible in many micrographs. Their observations were primarily carried out on planes parallel and close to the interface, rather than on fracture planes perpendicular to the interface where the massive CH is more strongly visible. It should be noted that the presence of massive CH of this kind, deposited out to distances of more than several microns from the interface, was shown to occur in GRC [12, 14], where observations were carried out on specimens fractured perpendicular to the fibre–cement paste interface.

The observations of Pinchin and Tabor [11] and Al Khalaf and Page [10] were also limited to surfaces exposed after breaking specimens at the interface. They reported that the paste zone around the interface was rich in CH and also remarked on the presence of porous areas of C–S–H and ettringite. It is not clear from their observations whether a continuous duplex film existed in contact with the steel surface in their specimens. It might be possible that during

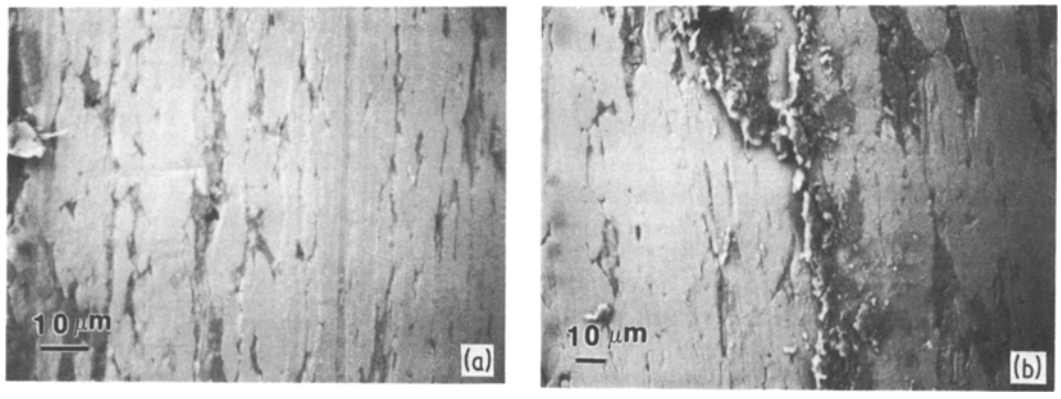


Figure 15 The surface of the steel fibre before being cast into the cement paste (a) and after being removed from the hardened paste (b), (c).

fracturing of the specimen this film is shattered and broken away from the surface. This may also account for the fact that such a film was rarely observed in the 3rd series of experiments in this work.

The present observations suggest that several different weak regions may exist in the zone around the interface. At the interface itself, the smooth layer of CH in the duplex film facing the steel is probably weakly bonded to the steel surface; a second zone of weakness is the region between the duplex film and the back-up paste, specifically in those local sections where no massive CH is deposited (see, for example, Figs. 6, 7b and 13a); the third weak region apparently identified is the porous transition zone backing the massive CH rim (see for example Fig. 12).

Thus, a crack initiated in the matrix and propagating toward the fibre, is likely to encounter as the first zone of weakness the region backing the CH rim. It is therefore likely to be arrested and to deviate at this zone, which is about 10 to 40 μm away from the fibre surface, giving rise to crack patterns as shown in Figs. 1a and b. If, however, the stress concentration is higher at the interface, as might be expected where shrinkage has occurred, the first weak

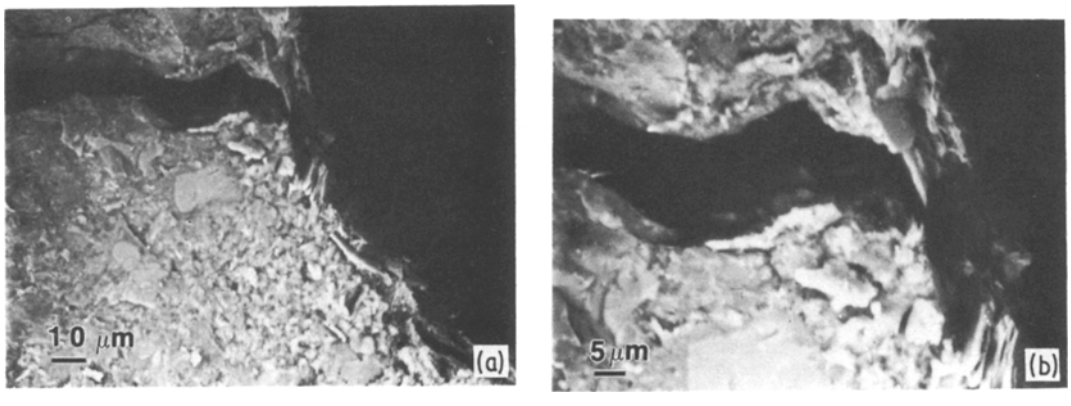
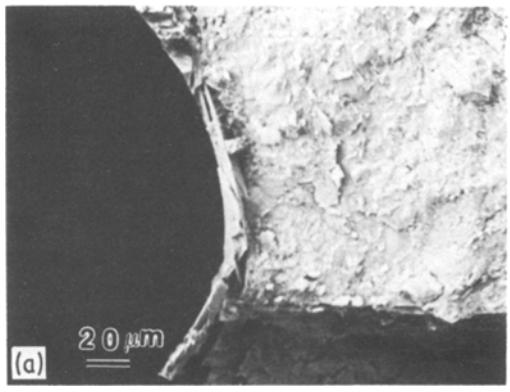
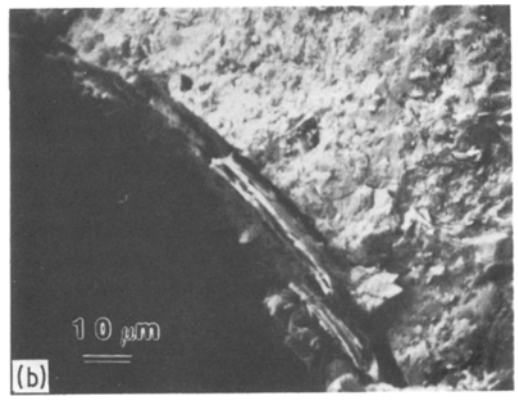


Figure 16 A crack initiated in the matrix and arrested and deviated at the CH layer rim around the fibre. (a) General appearance, (b) higher magnification of the zone of crack deviation.





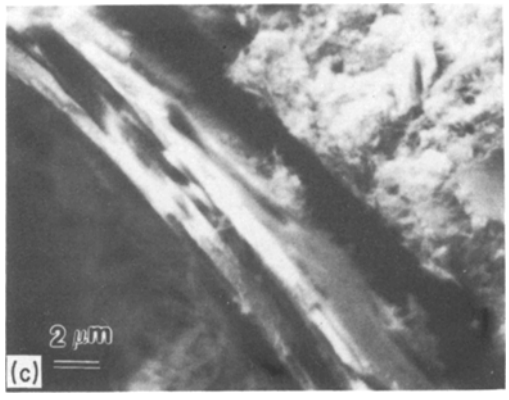


Figure 17 A crack initiated in the matrix and arrested and deviated at the CH layer rim around the fibre (a) general appearance, (b), (c) higher magnifications showing the separation between the CH rim and the paste around it.

zone to fracture would be the interface itself, giving rise to cracking patterns such as the one shown in Fig. 2.

Acknowledgement

The assistance of Mrs Janet Lovell in carrying out this work and her superb maintenance of the SEM are gratefully acknowledged.

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Received 24 July
and accepted 20 November 1984