JOURNAL OF MATERIALS SCIENCE 16 (1981) 1063–1070

Portland cement clinker viewed by transmission electron microscopy

G. W. GROVES
Department of Metallurgy and Science of Materials, University of Oxford, Parks Road, Oxford, UK

Thin sections of Portland cement clinker have been prepared by ion-beam thinning and examined in the electron microscope. The three most abundant phases, alite, belite and tricalcium aluminate have been identified. Features of interest include unexplained reflections in the diffraction patterns from alite and internally twinned or faulted martensite plates in belite. Hydrate gel coatings are obtained on the silicate phases but not on the aluminate phase, by immersing the thinned clinker in water. Dislocations in the aluminate phase do not appear to affect its reaction with water. On alite, easily observable hydrate coatings are obtained after immersion times as short as 5 min.

1. Introduction

The microstructure of Portland cement clinker has been studied by optical microscopy for many years. The four main phases, alite (impure C_3S), belite (impure C_2S), C_3A and C_4AF* can all be identified, but little can be seen of their internal microstructure, apart from striations seen on belite and attributed to twinning [1]. Cement hydration products in the form of dispersed particles have been studied by transmission electron microscopy (TEM) [2, 3]. The hydration of dispersed cement particles has been observed directly in an environmental cell by high-voltage TEM [4], but in this type of study the cement particle is usually too thick to allow its internal microstructure to be studied. The purpose of the present paper is to present the results of a study of ion-beam thinned Portland cement clinker. The microstructure of the three most abundant clinker phases, alite, belite and C_3A is determined in greater detail than has hitherto been achieved. In addition, thinned specimens have been hydrated for short times and gel coatings observed after periods as short as 5 min. It is believed that this technique will prove to be of considerable value in the study of the effect of the clinker phase microstructure and the composition of the hydrating solution on the early stages of hydration and thus may provide a valuable tool in understanding cement hydration.

2. Experimental procedure

Blue Circle (Northfleet) clinker was sectioned, ground, polished and ion-beam thinned following the same procedure as generally used for the preparation of thin specimens of ceramics (see e.g. [5]). Ion-beam thinning conditions were 5 kV, 60 to 90 microamp on two guns, tilt angle 15°. The main obstacle to the preparation of good specimens was the porosity of the clinker, and it was considered worthwhile to select those clinker pieces which appeared least porous; however, none were found in our samples which were not still very porous. Because of the uneven thinness of the final specimens it was a considerable advantage to examine them in the high-voltage electron microscope (HVEM), although some useful work has also been done at 100 kV [6]. An environmental cell [7] was used in the HVEM to study hydrate coatings formed on thin specimens without subjecting them to vacuum.

The identification of the cement clinker phases from electron diffraction patterns was aided in some cases by evaporating gold onto the surface of the thinned specimen, to provide accurate

---

*The abbreviations usual in cement chemistry are used: $C_2S = 2CaO SiO_2$, $C_3A = 3CaO Al_2O_3$ etc.

0022–2461/81/041063–08$02.80/0

calibration of the d-spacings and thus remove, as far as possible, the ambiguities which can arise from phases which have many closely-similar d-spacings.

Hydration of thinned clinker specimens was carried out by gripping the specimen, sandwiched between nickel grids, in stainless steel tweezers and immersing it in approximately 10 ml of water or another solution for a known period of time, after which the excess solution was drained off the specimen with filter paper.

3. Results and discussion

3.1. General

The three most abundant phases, alite, belite and C_3A were identified by electron diffraction. No other phase was detected, although some would be present in the clinker in low abundance, and indeed the ferrite phase C_4AF was detected in optical examination of sections by its characteristic colour. All three observed phases were stable in the electron beam (at either 100 kV or 1 MV) so that no special techniques were needed for their examination.

3.2 Alite

As would be expected from its highest relative abundance, alite is the most frequently detected phase. Many areas of alite are featureless, and these give clear diffraction patterns. These are of some interest because of an element of doubt about the crystal structure of alite. The usually accepted structure has the *C*-centred monoclinic lattice determined by Jeffery [8], with parameters $a = 3.308$ nm, $b = 0.707$ nm, $c = 1.856$ nm, $\beta = 94°10'$. (The precise values of the parameters will depend on the alite composition.) However Jeffery observed certain weak reflections on his X-ray rotation photographs, usually too weak to locate accurately in reciprocal space, which could not be accounted for on the basis of the above lattice. These led Jeffery to suggest that the true unit cell might be six times larger than the cell described above [8].

The electron diffraction patterns can generally be indexed on the basis of Jeffery's lattice, but several cases of extra reflections, usually but not always half-way between the reflections seen by Jeffery, have been observed. These do not seem to

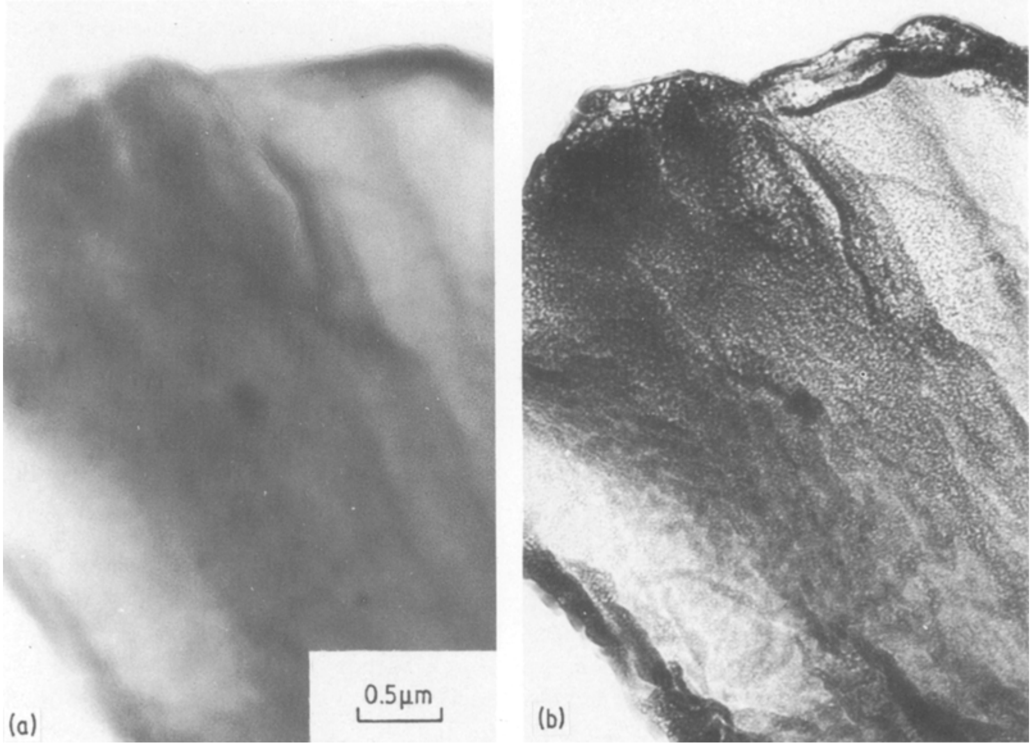


Figure 1 Coating formed by 5 min hydration of a thinned clinker in distilled water (a) in He at a pressure of 550 mm Hg (b) in a normal microscope vacuum.

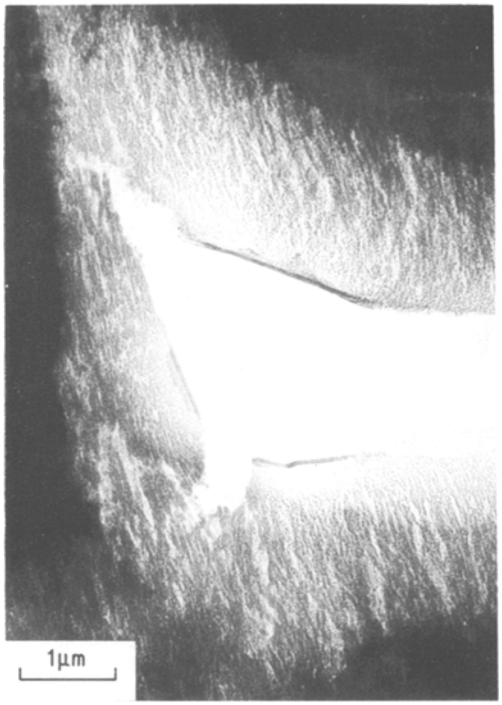


Figure 2 Gel coating formed by 5 min hydration of thinned clinker in distilled water. Phase identified as alite (darker region).

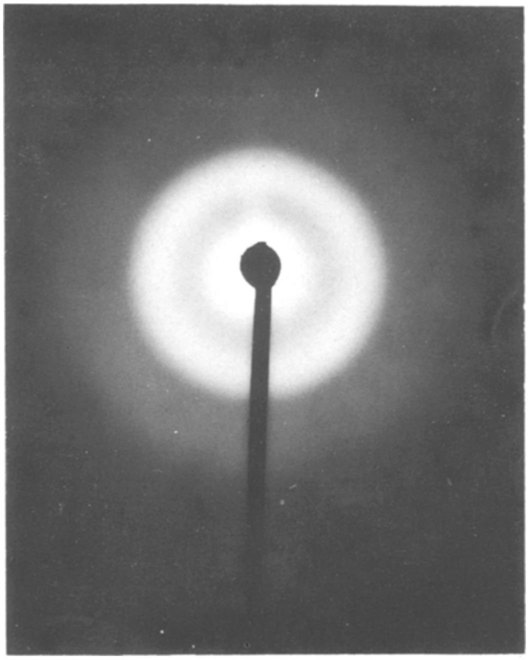


Figure 3 Diffraction pattern from a hydrate gel coating formed by dipping a thinned clinker into water.

arise from a larger true lattice but rather to be due to a defect structure not yet identified*. Further TEM work may finally solve this problem.

3.3. Hydration experiments

Gel coatings rapidly formed on thin specimens which were dipped in approximately 10 ml of water. An important question is whether or not the structure of these coatings is severely affected when they are examined in the electron microscope in the normal way. Some specimens were inserted in the environmental cell of the HVEM at near-atmospheric pressure immediately after hydration. After viewing at near-atmospheric pressure the chamber was progressively evacuated to determine whether this produced severe changes in gel coating structure. Fig. 1 shows that no gross changes occur on evacuation, although the resolution of the microscope at near-atmospheric pressure is not adequate to determine whether changes in fine structure occur. It appears that useful studies can be made even without an environmental cell, and subsequent micrographs (Figs 2 to 4) are taken from specimens inserted in the microscope in the normal way.

The water–cement ratio is very large in these experiments, and unless the composition of the hydrating solution is adjusted in an appropriate way during the course of hydration, the results at longer times may not correspond to events in normal clinker hydration. However, very short times of immersion produce easily observable coatings in thin specimens. Fig. 2 shows a coating produced on alite after 5 min immersion in distilled water. Apparently the alite is converted to hydrate gel *in situ* so that a thin, tapering edge will be converted to gel for a distance from the edge of about ($d \cot \theta/2$), where d is the depth of attack and θ is the angle of taper. The ($\cot \theta/2$) term is an effective magnification factor allowing quite small depths of conversion to be easily detected. Preliminary experiments have shown that the determination of gel and adjacent alite composition by energy-dispersive X-ray analysis combined with STEM is feasible, although the variablility of Ca and Si counts was too severe to allow quantitative results to be presented from these brief initial

---

*Twinning in alite has been observed optically [9] but has not been identified in the present work.

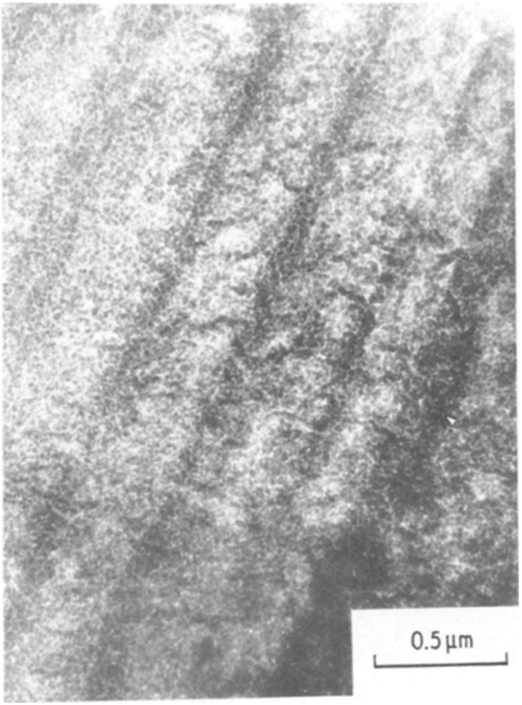


Figure 4 Banded structure in a gel sheet formed by immersion of thinned clinker for 45 min in tap water. Original phase not identified.

experiments. An interesting observation was that Cl was detected in the coating of a specimen hydrated in tap water, suggesting that Cl^- ions can be incorporated in the initial gel.

A further application of this technique is in the study of the effects of additives on the initial stages of hydration. For example, a 5 min immersion in a 16% solution of lead nitrate, a known retarder [10], produced a much more extensive gel coating than the same period of immersion in distilled water. It is possible that the long-term retarding action of lead nitrate is related to this effect.

A specimen hydrated for 45 min in water produced very extensive films of hydrate gel. The diffration pattern from such a film, Fig. 3, is the same as from the thinner initial coatings and the position of the diffuse rings of approximately 0.3 and 0.2 nm are in reasonable agreement with the diffuse X-ray peaks from C_3S paste [11]. One area of the gel film showed an interesting banded structure (Fig. 4). Although the original phase had not been observed, the banded appearance is very suggestive of twin bands, replicated in the gel, which would imply that the *in situ* conversion of the phase to hydrate gel was related to the crystallographic orientation of the phase.

3.4 Belite

The usual structure of C_2S in cement clinker is the monoclinic β form [12], $a = 0.5507$ nm, $b = 0.6754$ nm, $c = 0.9317$ nm, $\beta = 94°37'$. (The lattice parameters will of course vary with the composition of the impure C_2S-forming belite in clinker.) Simple twin bands have been seen in a TEM micrograph of a fragment of C_2S [13]. Banded structures are readily visible in the optical microscopy of belite in clinker [1]. However, Fig. 5 shows that belite can have a fine structure on a scale not resolvable by optical microscopy. In spite of the complex appearance of this microstructure the diffraction pattern (Fig. 5) shows that most of the diffracting material has the [100] direction parallel to the electron beam. The striations running across the lamellae are parallel to [010] and are therefore due to faults or small twin bands on $(h0l)$ planes [both (100) and (001) being possible]. The lamellae themselves do not appear to be in any simple rational orientation and it should be noted that there are two lamellae orientations each with the same striation orientation. Fig. 6 from another area of the same specimen, shows what appear to be internally twinned plates. The diffraction in this case showed many reflections and only the (010) spacing was clearly identifiable; the orientation of this showed that the internal twin bands were again on $(h0l)$ planes. Again there are two orientations of plate with a single type of internal twin. Yamaguchi and Takagi [14] described structures in belite, observed by transmitted light, which may correspond, on a coarser scale, to the above observations. Their interpretation was that two sets of twins were formed, the first during the transformation of a trigonal α-phase of C_2S to an α'-orthorhombic-phase, at about 1400° C, the second during a lower temperature transformation of α' to the monoclinic β phase, at 680° C. However, Figs 5 and 6 are not consistent with the larger lamellae being formed by twinning since all the finer bands within them have the same orientation. The structures are, however, consistent with their formation by a martensitic transformation. The small atom displacements required to convert α to α' or β and α' to β [12] suggest that these transformations might occur martensitically. In oxide systems at least one martensitic transformation has been well established, namely that occurring in zirconia [15]. The essence of the martensitic transformation is that a strain produced by slip, twinning or faulting is

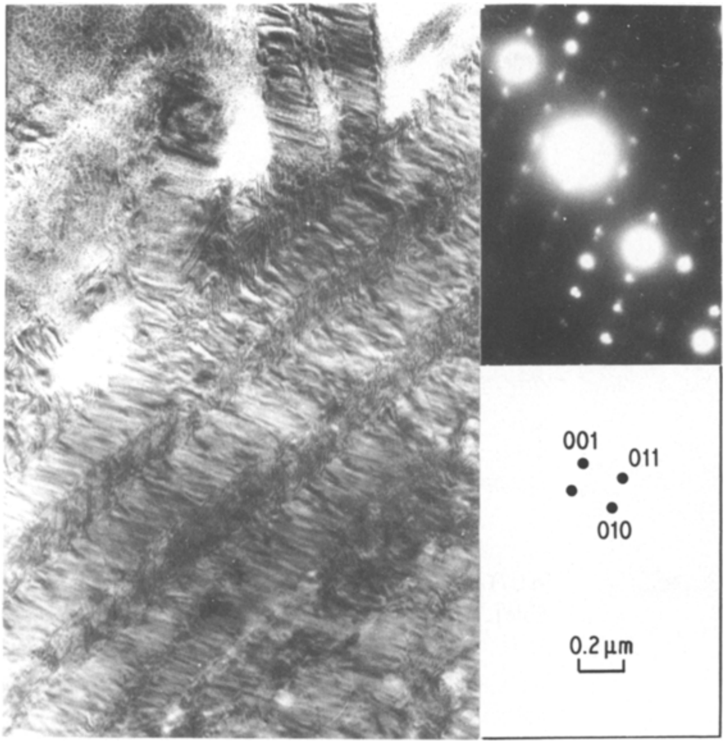


Figure 5 Internally twinned or faulted lamellae in belite. The electron diffraction pattern is shown in the correct orientation and the β-C_2S indices of three of the innermost reflections are shown. 001 and 010 are forbidden by the $P2_1/n$ space group which requires $h + l$ to be even in $h0l$ reflections and k to be even in $0k0$, but they can occur nevertheless by double diffraction e.g. $012 + 00\bar{2} = 010$. Indexing as α'-phase would also be possible, although the existence of this phase is less likely.

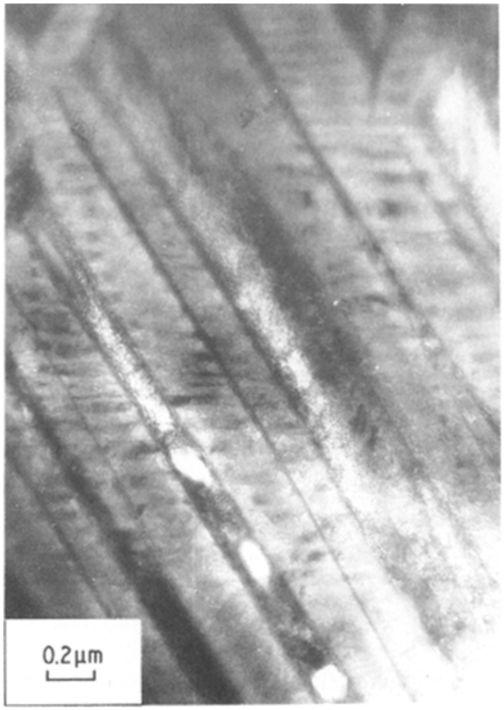
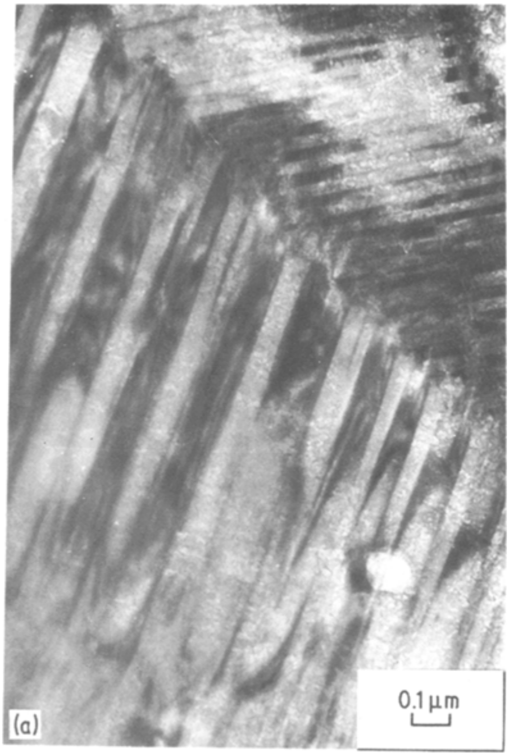


Figure 6 Internally twinned lamellae of belite.

added to the lattice strain that converts one phase into the other in order to produce a macroscopically undistorted interface between converted and as yet unconverted phases, which forms the habit plane of (usually) lamellae of transformed material. This habit plane is generally irrational and up to four habit plane solutions arise for a given type of slip, twinning or faulting [16]. Figs 5 and 6 are entirely consistent with these features.

Belite forms a gel coating on immersing the thinned specimen in water, although it is less extensive than the coating formed in the same time on alite. Figs 5 and 6 are in fact from specimens immersed for 30 min in water and some gel coating in a thinner region can be seen in a corner of Fig. 5. The specimen shown in Fig. 6 appears to have suffered preferential attack in interlamellar regions.

A simpler form of twinning is also exhibited by belite. Fig. 7a shows a banded area (this specimen was also hydrated and there is a fine scale surface structure due to the reaction with water which however does not affect the following discussion). The diffraction pattern, Fig. 7b, was taken from an area that encompassed both sets of bands in Fig. 7a. The larger bands provide the stronger reflections and the key in Fig. 7b shows how these



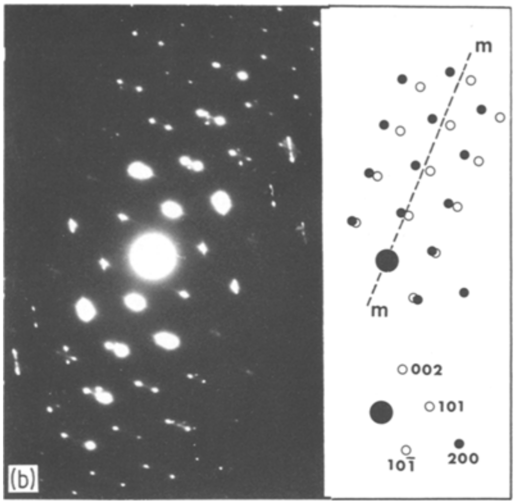


Figure 7 (a) Twin bands in belite and (b) electron diffraction pattern corresponding to (a). The specimen was tilted very slightly between (a) and (b) to equalize the intensities of the twin-related reflections. The key shows the two sets of reflections depicted by closed and open circles which are related by the mirror plane m–m which is parallel to the broader bands. The β-C_2S indexing for the open circle reflections is shown at the bottom of the key; indexing as β rather than α' is unambiguous in this case. The 2 0 0 reflection is common to both sets, indicating a (1 0 0) composition place for the twins. (In this case, with the electron beam parallel to 0 1 0, the forbidden 0 0 1 and 1 0 0 reflections cannot arise by double diffraction.)

arise from two reciprocal lattices, mirror images of one another in a plane parallel to the bands. In other words the bands are simple reflection twins with a (100) composition plane. This is the same type of twinning as that identified by Jelenic *et al.* [13], who postulated that it arose during transformation of orthorhombic α'-C_2S to monoclinic β, with a mirror plane of the orthorhombic lattice becoming the (100) β twinning plane. Fig. 7 suggests a slightly different explanation. Fig. 7b shows a second twin related set of reflections, with the mirror plane at 120° to that of the first set, evidently arising from the smaller twin bands in the upper right hand corner of Fig. 7a. When the points at the centres of the groups of twin-related reflections are marked out, they constitute a hexagonal set of points within the accuracy of the construction. The simplest explanation of Fig. 7 is then that at elevated temperature a hexagonal lattice was present over the whole area shown in Fig. 7a. On cooling the clinker a transformation to the monoclinic lattice of β-C_2S occurred. The *c*-axis of the hexagonal phase transformed unchanged into the *b*-axis of the monoclinic phase (2nd setting) and this axis is parallel to the electron beam in Fig. 7. The transformation of the lattice in the plane normal to this axis was accomplished by a simple shear, parallel to a mirror plane of the hexagonal lattice (m–m in Fig. 7b). The mirror image of this shear i.e. an equal and opposite shear also transforms the lattice and by alternating the shear and its reverse in bands, twin-related bands of β were formed of equal thickness, giving zero net strain for a transforming volume. This is the simplest type of martensitic transformation. In the two regions of Fig. 7a a different choice of mirror plane was made. The production of Fig. 7 by the transformation of an orthorhombic phase is a little less easy to explain although it could be argued that the orthorhombic phase was sufficiently close to the hexagonal one that essentially the above argument could be applied, or that the two regions of Fig. 7a came in fact from regions of α', differently, but coincidentally, orientated.

An obvious question to discuss is why different regions of belite should show markedly different transformation microstructures, as in Figs 5 and 7. Very probably the explanation of this difference lies in a difference in the lattice strains involved. The simplest form of martensitic transformation exhibited by Fig. 7 requires one axis in the lattice to remain invariant, becoming the *b*-axis of β-C_2S. If a change in the length of this axis is required, a three-dimensional strain is needed, bringing in the more general type of martensitic structure seen in Figs 5 and 6. An explanation for this difference in lattice strain is more speculative. One possibility is that the phases involved are different. The diffraction pattern of Fig. 5 could be indexed as α'-C_2S; it has been indexed as β on the grounds of the known greater probability of this phase in clinker. It can be speculated that Fig. 5 represents the α to α' transformation and Fig. 7, where the identificaion of β-C_2S is unambiguous, represents α to β or possibly α' to β. There are obviously other possibilities and the spread in the published values of the lattice parameters of the phases [12] and the unknown composition of the belite make a final conclusion impossible at this stage.

3.5 Tricalcium aluminate

The structure of C_3A is cubic, lattice parameter = 1.52 nm [17]. It usually appears featureless, giving clear, undisturbed diffraction patterns. In one specimen a complex fine precipitate, probably decorating dislocation lines, was observed (Fig. 8). This was the only observation in our clinker of a fine precipitate in any phase and it appears that the impurities present in clinker are generally held in solution in the phases. Regions identified as C_3A did not appear to form a hydrate gel coating on immersion in water. The specimen shown in Fig. 9 was immersed in distilled water for 5 min. It is notable that there is no sign of preferential attack (e.g. pitting) at the points where the dislocation lines meet the surface so that the only direct evidence on the effect of lattice defects on hydration rates is so far negative.

3.6 Regions of complex microstructure

Certain regions of clinker, not common but not extremely rare, exhibited a complex and highly disordered microstructure whose diffraction patterns have defied complete solution. An example of such a region, containing many apparent faults, and regions of Moiré fringes indicating misorientations, is shown in Fig. 10. The corresponding diffraction pattern exhibited a large number of reflections and could not be completely

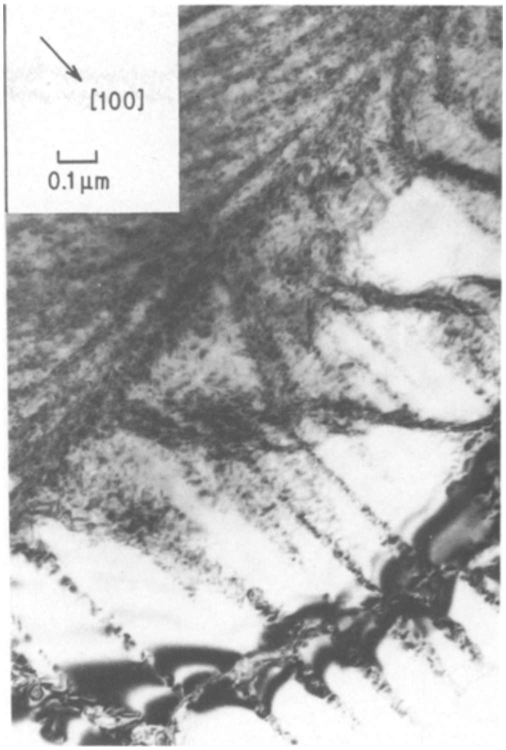


Figure 8 Precipitates in tricalcium aluminate.

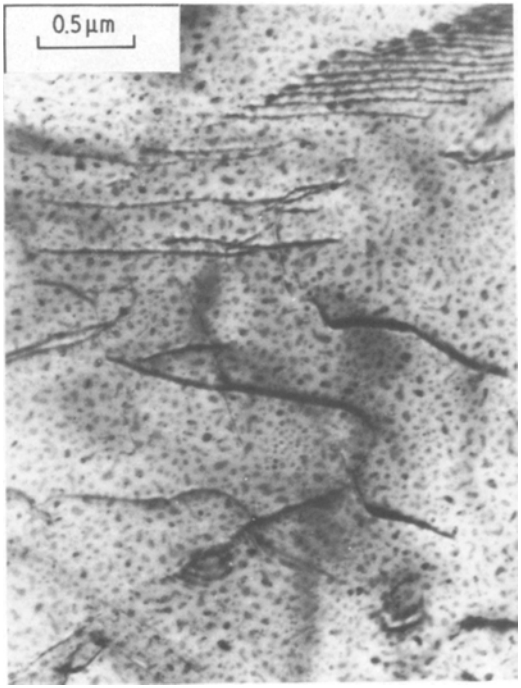


Figure 9 Dislocations in the tricalcium aluminate phase in a thinned clinker immersed in distilled water for 5 min. The surface structure is due to a gold coating evaporated onto the specimen after its immersion in water. The electron beam is parallel to $[23\bar{3}]$.

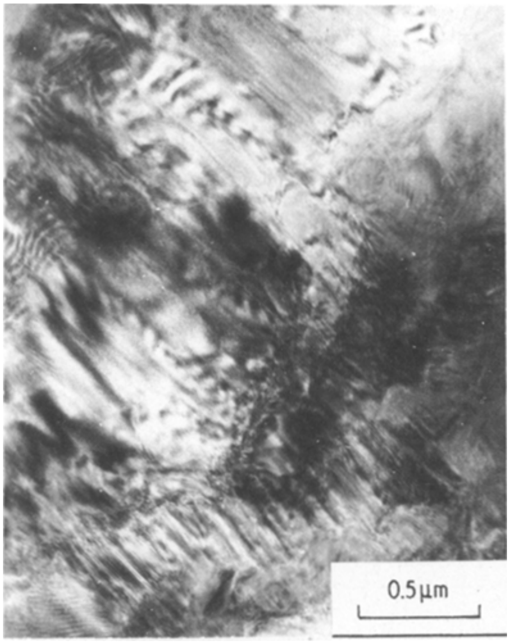


Figure 10 Region of complex microstructure.

solved, although one repeat spacing indicated that very probably alite was present. It is plausible to suggest that such regions might be subject to more rapid hydration but there is as yet no direct evidence of this.

4. Summary and conclusions

The overall impression of the microstructure of the Blue Circle (Northfleet) clinker examined is that many regions are free of obvious defects. The dislocation density is generally low (dislocation will of course be introduced when the clinker is ground to make cement powder). The most prominent defects are twin bands which are sometimes seen covering wide areas. Internally twinned or faulted plates have been seen in belite, which strongly suggest that some at least of the belite undergoes a martensitic transformation when the clinker is cooled. Immersion of thinned specimens in water produces hydrate gel coatings on the silicate phases which do not appear to be unduly sensitive to the electron microscope environment. On alite, times as short as 5 min produce readily observable coatings. A known retarder, lead nitrate, produces an increased coating. On C_3A coatings are not observed and dislocations in C_3A do not appear to influence the reaction with water.

This preliminary investigation leaves many questions unanswered but demonstrates the feasability of a powerful technique for examining the microstructure of cement clinker, and the effects of clinker microstructure and solution composition on the early stages of cement hydration.

Acknowledgements

The author is grateful to Dr D.D. Double for first engaging his interest in the subject of cement, and for continued valuable discussion. The financial support of the Science Research Council is acknowledged.

References

1. F. M. LEA, "The Chemistry of Cement and Concrete" (Edward Arnold, London, 1970) p. 102.
2. A. GRUDEMO in "The Chemistry of Cements" Vol. 1, edited by H. F. W. Taylor (Academic Press, London 1964) p. 371.
3. J. A. GARD in "The Chemistry of Cements" Vol. 2, edited by H. F. W. Taylor (Academic Press, London, 1964) p. 243.
4. D. D. DOUBLE, A. HELLAWELL and S. J. PERRY, *Proc. Roy. Soc.* **A359** (1978) 435.
5. D. J. CLINTON, *Micron* **3** (1972) 358.
6. D. PEARSON, thesis submitted for Part II Examination in Metallurgy and Science of Materials, University of Oxford, 1980.
7. H. M. FLOWER, N. J. TIGHE and P. R. SWANN, "High Voltage Electron Microscopy", edited by P. R. Swann, C. J. Humphreys and M. J. Goringe (Academic Press, London, 1974) p. 383.
8. J. W. JEFFERY, *Acta Cryst.* **5** (1952) 26.
9. Y. ONO, S. KAWAMURA and Y. SODA, Proceedings of the International Symposium on the Chemistry of Cement (Cement Association of Japan, Tokyo, 1968) Vol. 1, p. 275.
10. W. LIEBER, Proceedings of the 5th International Symposium on the Chemistry of Cement (Cement Association of Japan, Tokyo, 1968) Supplementary paper II – 22.
11. H. W. F. TAYLOR in "The Chemistry of Cements" Vol. 1, edited by H. W. F. Taylor (Academic Press, London, 1964) p. 183.
12. F. M. LEA "The Chemistry of Cement and Concrete" (Edward Arnold, London, 1970) p. 322.
13. I. JELENIC, A. BEZJAK and M. BUJAN, *Cement Concrete Res.* 8 (1978) 173.
14. G. YAMAGUCHI and S. TAKAGI, Proceedings of the Fifth International Symposium of the Chemistry of Cement (Cement Association of Japan, Tokyo, 1968) Vol. 1, p. 181.
15. G. K. BANSAL and A. H. HEUER, *Acta Met.* **22** (1974) 409.
16. C. M. WAYMAN, "Introduction to the Crystallography of Martensitic Transformations" (Macmillan, New York, 1964).
17. P. MONDAL and J. W. JEFFERY, *Acta Cryst.* **B31** (1975) 689.

Received 26 August and accepted 10 October 1980.