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# High-resolution electron microscopy study of belite

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The microstructures of belite examined by high-resolution electron microscopy (HREM) show the (1 0 0) and (0 0 1) twin lamellae which are introduced by shear stresses during the transformation of $\alpha'$-$C_2S$ to $\beta$-$C_2S$. $\gamma$-$C_2S$ formed in the larnite was identified and the orientation relationship between them was also determined by a composite electron diffraction pattern (EDP), which is different from that suggested earlier by Groves. The EDP and the HREM image showed the existence of the unstable phase $\alpha'_L$-$C_2S$.

## 1. Introduction

As an important constituent in cement clinker, belite ($Ca_2SiO_4$ or $C_2S$) has been extensively studied in the past by optical microscopy and X-ray diffraction methods. The relationships of transformation among these four phases $\beta$-$C_2S$, $\gamma$-$C_2S$, $\alpha'$-$C_2S$ and $\alpha$-$C_2S$ have been discussed by Smith *et al.* [1]. Normally belite occurs in the monoclinic $\beta$ form and its structure was determined by Midgley [2]. Its property of hydration was found to be affected by the addition of impurities [3] though its microstructural change was still not clear. Recently transmission electron microscopy (TEM) has also been used to study these phases. Groves [4, 5] studied the (1 0 0) twin lamellae and the dislocations at the twin domain boundary of the $\beta$-$C_2S$, which were formed from $\alpha$-$C_2S$ or $\alpha'$-$C_2S$, respectively, in the cement clinker during cooling (see Table I). He suggested that the transformations from $\alpha$-$C_2S$ or $\alpha'$-$C_2S$ to $\beta$-$C_2S$ are martensitic and only small displacements of the atoms are needed. The twin lamellae result from the shear strain of this martensitic transformation. Ghose and Barnes [6] examined twin lamellae with the (1 0 0) twin plane of the $\beta$-$C_2S$ in Portland cement clinker by high-voltage electron microscopy. High-resolution electron microscope (HREM) can give more insight into the microstructure of clinker at the unit cell level, and this was carried out by us with a JEM-200CX electron microscope with a point-to-point resolution of 0.25 nm. The microstructures and the defects in them are presented in the following.

## 2. Experimental procedure

Dicalcium silicates were formed by mixing carbonate of lime, silicon dioxide and a small portion (~ 1%) of potassium superoxide or sodium superoxide powder, pressing the powder mixture in a cylindrical mould at about 150 MPa, and finally sintering the resultant compact pieces (about 20 mm × 10 mm) in a platinum boat in air at 1350° C for about 8 h. The sintered specimens were then air-cooled after withdrawal from the furnace. The specimens were white and brittle so that they could be easily ground into fragments in an agate mortar. A drop of a suspension of fragments in absolute alcohol was put on a holey carbon film on a microgrid in order to be examined in the electron microscope after drying. The addition of potassium superoxide was aimed at doping the dicalcium silicates and in the mean time to stabilize the larnite.

## 3. Results and discussion

$\beta$-$C_2S$ is the most abundant phase in the clinker, though small amounts of $\gamma$-$C_2S$ and $\alpha'$-$C_2S$ have also been detected by electron diffraction. The specimens were sensitive to electron beam irradiation, and could last 30 min at a beam current density of 8 pA $cm^{-2}$ but only several seconds at 20 pA $cm^{-2}$. The bonds are weak in belite and the structure is easily deteriorated into the amorphous state by irradiation damage. Therefore we have to use a low beam current density to protect specimens from irradiation damage and an image intensifier was used to solve this problem.

### 3.1. $\beta$-$C_2S$

The belite usually found in cement clinker is in the monoclinic $\beta$ form and its space group is $P2_1/n$ [2]. The projection along the unique $b$ axis is shown in Fig. 1, where the structure may be regarded as a composite

TABLE I Phases in belite

| Type | Symmetry | Cell parameters | | | |
|---|---|---|---|---|---|
| | | $a$ (nm) | $b$ (nm) | $c$ (nm) | $\beta$ (deg) |
| $\alpha$ | Trigonal | 0.5526 | | 0.7307 | |
| $\alpha'_H$ | Orthorhombic | 0.5490 | 0.9260 | 0.6750 | |
| $\alpha'_L$ | Orthorhombic | 1.1070 | 1.880 | 0.6850 | |
| $\beta$ | Monoclinic | 0.5480 | 0.6670 | 0.9280 | 94.6 |
| $\gamma$ | Orthorhombic | 0.5078 | 1.1230 | 0.6750 | |

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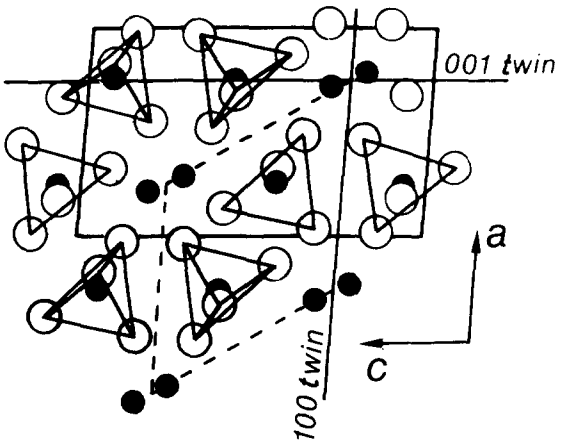


*Figure 1* Projection along the $b$ axis of $\beta$-$C_2S$ with possible twin planes (shown by lines) and a pseudo-hexagonal cell (shown by dashed lines): (●) calcium, (○) oxygen (after Midgley [2]).

of strings of alternating calcium ions and isolated $SiO_4$ tetrahedra in the $b$ direction which are linked by the remaining calcium ions in the holes left between the tetrahedra. The silicon and calcium atoms lie close to the $x = \frac{1}{4}$ plane. Only a small shift of these atoms and a small rotation of the tetrahedra is necessary to produce orthorhombic symmetry. These small adjustments correspond to the phase transformation from $\alpha'$ to $\beta$ and thus explain the polysynthetic twinning on (1 0 0) or (0 0 1) twin planes which are indicated by lines in Fig. 1.

A rather larger distortion is required in order to produce trigonal symmetry. This corresponds to the phase change from $\alpha$ to $\beta$ and the pseudo-hexagonal cell is shown by broken lines. The electron diffraction pattern of the (1 0 0) reflection twins of $\beta$-$C_2S$ is shown in Fig. 2, where $h\,0\,0$ diffraction spots with $h$ odd appear owing to multiple diffraction. The corresponding HREM image (Fig. 3) shows that the unit cells, outlined by white lines, are arranged in the (1 0 0) mirror reflecting positions. Stacking faults, which could be caused by lattice shear strain during the phase transformation from $\alpha'$ to $\beta$ during cooling of the clinker [5], form at the interface (indicated by arrows). During the transformation from $\alpha'$ to $\beta$, (1 0 0) twinning may be produced because a pair of shear stresses, equal in magnitude and opposite in

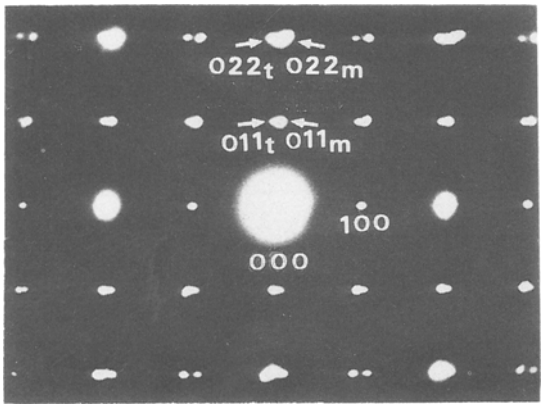


*Figure 2* An [0 $\bar{1}$ 1] zone EDP of $\beta$-$C_2S$ showing (1 0 0) twins. The forbidden reflections $h\,0\,0$ with $h$ odd appear as a result of multiple diffraction.

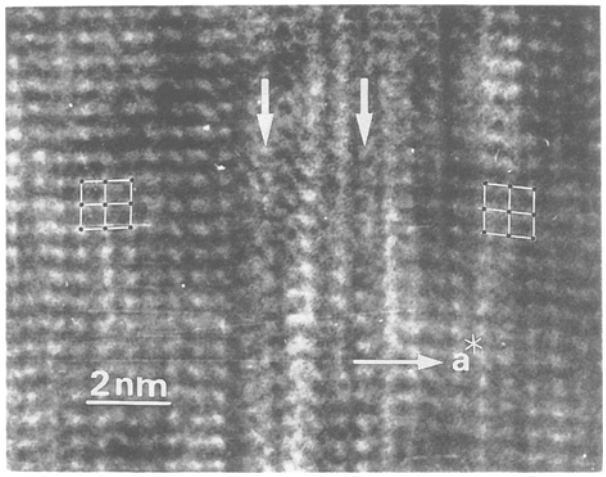


*Figure 3* [0 $\bar{1}$ 1] HREM image demonstrating the (1 0 0) twins in $\beta$-$C_2S$ with the unit cells outlined. Stacking faults at the interfaces are indicated by arrows.

direction, could arise and cause a small rotation of the $a$ axis from its original into its new position [5]. On the other hand, some intermediate state in the phase transformation may exist and the lattice shear may cause dislocations as well as stacking faults, which were not observed by optical and X-ray methods before but could be shown in the HREM image.

The indices of the diffraction spots due to the twin, in terms of the matrix reciprocal lattice, can be deduced from the formula given in the literature [7]. After twinning, $h\,k\,l$ becomes $h'\,k'\,l'$ and

$$h' = \bar{h} + 0.09\bar{l} \quad k' = k \quad l' = l$$

for (1 0 0) twins (1)

$$h' = h \quad k' = k \quad l' = \bar{l} + 0.25\bar{h}$$

for (0 0 1) twins (2)

Therefore the indices of diffraction spots due to the (1 0 0) twin in Fig. 2 can be expressed in terms of the matrix spots by Equations 1. From Equation 2 it is clear that the $h'\,k'\,l'$ spots of the twin can be obtained by moving the $h\,k\,l$ spots of the matrix along the [0 0 1]* direction by $(0, 0, 2\bar{l} + 0.25\bar{h})$ and for the spots with $h = 4n$ ($n$ is an integer), the spots of the twin's $h'\,k'\,l'$ are all integers and coincident with those of the matrix. Consequently the $\frac{1}{4}$ spots of the matrix and the twin are coincident. Fig. 4 is an electron diffraction pattern showing this case, though the spots with $h = 4n$ belonging to both the matrix and twin do not appear in this pattern. However, for the $h \neq 4n$ rows the separation of spots is a multiple of $\frac{1}{4}$[0 0 1]*.

Although it has been predicted before that (0 0 1) reflection twins could possibly be present in the $\beta$ phase [6], no experimental evidence of this has been reported yet. In addition, Fig. 5 is the corresponding HREM image showing the (0 0 1) twin-related reflection structure of $\beta$-$C_2S$ and their outlined unit cells. There is a smooth interface (indicated by arrows) connecting the two twin variants and stacking faults also arise from the shear strain of lattice transformation. This is quite similar to the case of the (1 0 0) twin. Following the mechanism of the (1 0 0) twin [5], it can be assumed that a pair of shear stresses, parallel

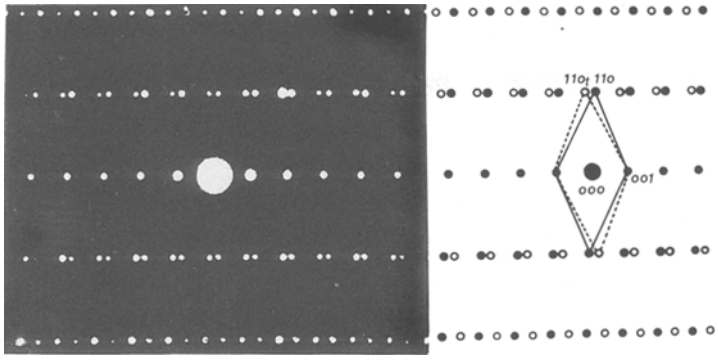


*Figure 4* A [1 $\bar{1}$ 0] zone EDP of $\beta$-$C_2S$ showing (0 0 1) twinning; (○) twin, (●) matrix.

to the $a$ axis of the $\alpha'$-$C_2S$, causes a small rotation of the $b$ axis of the $\alpha'$-$C_2S$ into the $c$ axis of $\beta$-$C_2S$ during the transformation from the $\alpha'$ to the $\beta$ phase as shown in Fig. 6. Because the $c$ parameter (0.928 nm) is much larger than $a$ (0.548 nm) in the $\beta$ phase, it is reasonable to believe that the energy for the formation of the (0 0 1) twin should be higher than that of the (1 0 0) twin, and this explains why the (1 0 0) twin is easily found in the $\beta$ phase. For comparison, pure dicalcium silicate was also examined by HREM and a twin structure could hardly be found in the $\beta$-$C_2S$. This implies that impurities in belite may favour twin and defect formation in the larnite.

### 3.2. $\gamma$-$C_2S$

The $\gamma$-$C_2S$ phase is present only in a very small amount in the clinker and it is unhydraulicity. Therefore, it is less important compared with $\beta$-$C_2S$. The structure of $\gamma$-$C_2S$ is orthorhombic and its space group is Pbnm [8]. It is of interest to study the coexistence and orientation relationship between the $\beta$ and $\gamma$ phases in cement clinker, because they have different hydration properties and would affect the performance of the cement. The orientation relationship between them, useful in the determination of intergrowth and transformation of the $\beta$ to $\gamma$ in the clinker, can be obtained from Fig. 7, which is a composite electron diffraction pattern of (0 1 1)* of the $\beta$ phase with (1 0 0) twin lamellae and (2 $\bar{1}$ 0)* of the $\gamma$ phase. Their indices are given in the schematical diagram, from which the following orientation relationships can be derived:

$$(1\,0\,0)_\beta \parallel (1\,2\,2)_\gamma$$

$$(0\,1\,\bar{1})_\beta \parallel (1\,2\,\bar{2})_\gamma$$

$$[0\,1\,1]_\beta \parallel [2\,\bar{1}\,0]_\gamma$$

This relationship is different from the $(0\,1\,0)_\beta \parallel (0\,0\,1)_\gamma$ assumed by Groves [9] when he studied the mechanism of the $\beta$ to $\gamma$ phase change. Fig. 8 shows the coexistence of these phases in which the dark contrast at the interface is possibly caused by the shear stress of transformation from $\beta$ to $\gamma$ phase.

### 3.3. $\alpha'$-$C_2S$

Two kinds of structure were determined in $\alpha'$-$C_2S$: $\alpha'_H$ is orthorhombic with $a = 0.549$, $b = 0.926$, $c = 0.675$ nm and its space group is Pmcn; $\alpha'_L$ has atoms arranged very similarly to $\alpha'_H$ but its $a$ and $b$ parameters are about twice as large as those of $\alpha'_H$ ($a = 1.107$, $b = 1.880$, $c = 0.685$ nm) and its space group becomes $Cmc2_1$ [10, 11].

Although it is considered to be less likely to be present in the clinker, the EDP shown in Fig. 9 can only be indexed based on the parameters of $\alpha'_L$. The streakings along the $b$ axis of the phase in the EDP in Fig. 9 was possibly due to faults in the specimen, which can clearly be seen in the corresponding HREM image shown in Fig. 10. Layers with periods of 0.9 and 1.8 nm are present, implying that there is a basic unit of 0.9 nm, possibly being the (0 1 0) plane of the $\alpha'_H$ phase. Therefore, polytypes with periods $b = n \times$

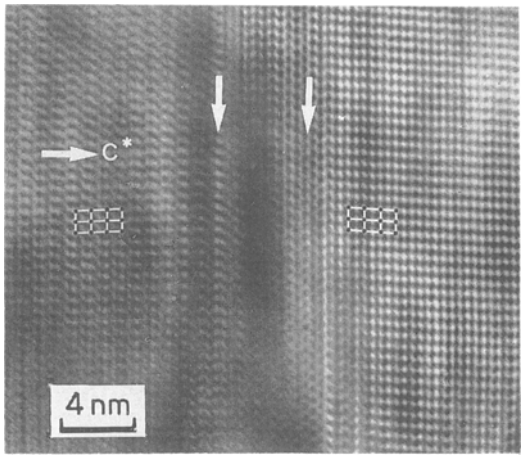


*Figure 5* [1 $\bar{1}$ 0] HREM image exhibiting an (0 0 1) twin with the unit cells outlined and the dislocations at the interface indicated by arrows.

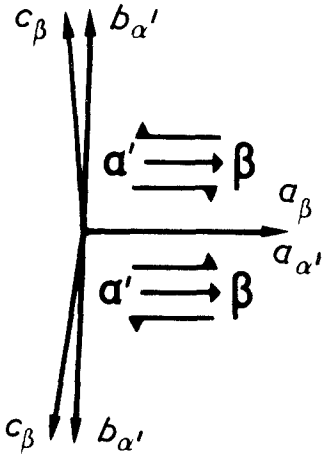


*Figure 6* Schematic diagram showing the (0 0 1) twin structure produced by pair of shear stresses, equal in magnitude but opposite in direction, during the transformation of $\alpha'$-$C_2S$ to $\beta$-$C_2S$.

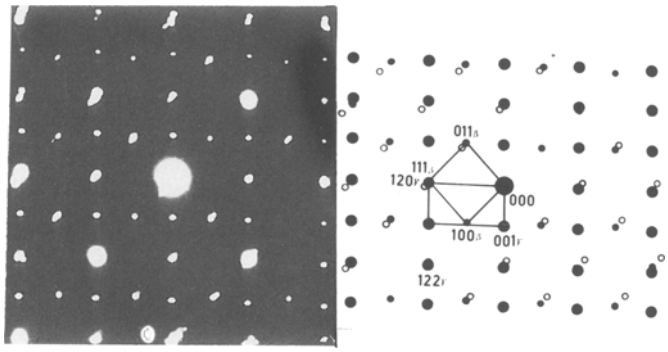


*Figure 7* A composite EDP of $(0\,1\,1)^*$ of $\beta$-$C_2S$ and $(2\,\bar{1}\,0)^*$ of $\gamma$-$C_2S$ with an indexed schematic diagram showing the orientation relationships between them: (●) $\gamma$, (●) $\beta$ matrix, (○) $\beta$ twin.

0.9 nm, ($n$ = 1 and 2) can coexist. The presence of stacking faults and various polytypes may possibly stabilize the $\alpha'_L$ phase and prevent it from transforming to $\beta$-$C_2S$ after cooling. This is perhaps the reason why a small amount of $\alpha'_L$-$C_2S$ remained in the clinker.

## 4. Conclusions

The existence of (0 0 1) twin structure in $\beta$-$C_2S$ has been proved by EDP and HREM images, and stacking faults caused by shear stresses appear at the interface of the twin lamellae. A new orientation relationship obtained from the composite EDP of $\beta$-$C_2S$ and $\gamma$-$C_2S$ has been found. Stacking faults and various polytypes found in the $\alpha'_L$ phase are possibly favourable to its existence in the clinker.

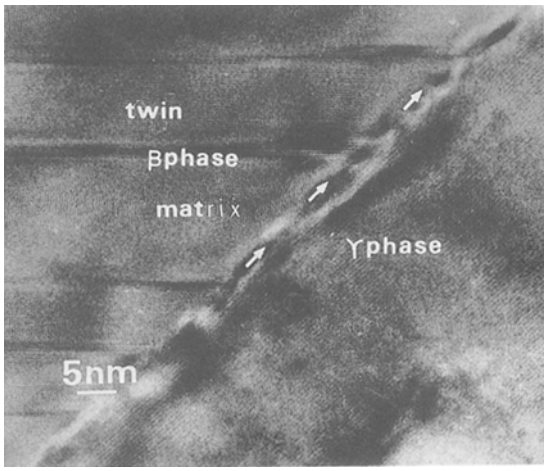


*Figure 8* A general view of the intergrowth of $\beta$ and $\gamma$ phases as well as the twin structures. The different contrast at the phase boundary marked by arrows is caused by the shear strain of the phase transformation.

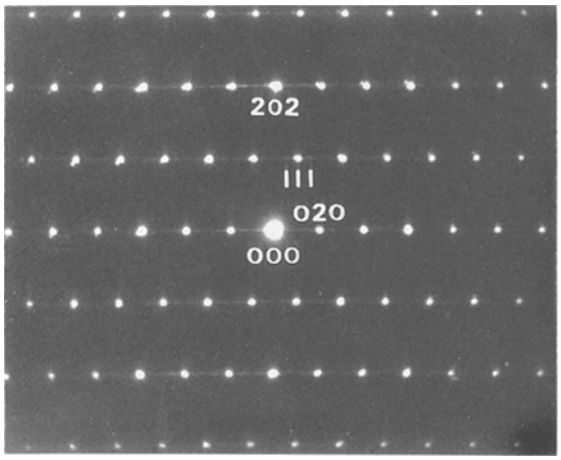


*Figure 9* An $[1\,0\,\bar{1}]$ zone EDP of $\alpha'_L$-$C_2S$ showing evidence of this phase existing in the clinker, and streaking along the $b$ axis.

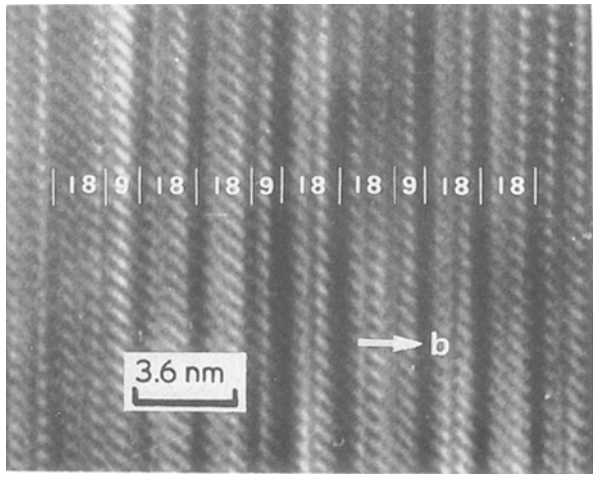


*Figure 10* $[1\,0\,\bar{1}]$ HREM image showing stacking faults with periods of 0.9 and 1.8 nm along the $b$ axis in the $\alpha'_L$-$C_2S$.

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