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Phase transformations in dicalcium silicate

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The $\beta \rightarrow \gamma$ transformation in dicalcium silicate has been studied by a combination of optical microscopy and transmission electron microscopy (TEM). The γ-phase forms as long needles or laths whose long axis is parallel to [001] γ. These tend to occur in bundles. TEM shows that regions of γ in partially transformed specimens are not internally twinned but contain a high density of dislocations and of low angle grain boundaries running parallel to the long axis of the particles. γ particles can be induced to form by the stress near a microhardness indentation. The nature of the $\beta \rightarrow \gamma$ transformation and the effect of the very large dilatation (14%) which accompanies the transformation are discussed. The $\alpha' \rightleftarrows \beta$ transformation has been studied on a TEM hot stage. It is confirmed that (100) β twins are formed on cooling through the $\alpha' \rightarrow \beta$ transformation temperature. Local stresses set up at the intersection of twin lamellae with domain boundaries are relaxed by slip on (100).

1. Introduction

Dicalcium silicate, C_2S*, is the second most abundant component of Portland cement clinker and is itself of potential interest as a cement-forming material requiring low temperature for its preparation [1]. Polymorphic transformations in C_2S have been studied, particularly by X-ray diffraction and differential thermal analysis (DTA) techniques [2–6]. The phases of particular concern in this paper are α', stable between 670 and 1420° C, β which probably has no region of thermodynamic stability at atmospheric pressure but which is nevertheless the polymorph into which α' transforms on cooling to about 670° C and which is usually present in cement clinker, and γ, the stable low-temperature polymorph. The γ phase has a 14% greater volume than the β phase from which it forms and this very large dilatation causes bodies undergoing the transformation $\beta \rightarrow \gamma$ to break up into small particles, a phenomenon known as "dusting". The reverse transformation, $\gamma \rightarrow \beta$ has never been observed, which is the ground for believing that β is not a stable phase. The $\beta \rightarrow \gamma$ transformation has been reported as occurring at temperatures below 500° C, but as being variable, under some conditions being rapid and under others not going to completion even with cooling to liquid nitrogen temperature [3]. The transformation is readily suppressed by impurities such as Cr_2O_3, B_2O_3, Na_2O and K_2O [2] and in Portland cement clinker the C_2S normally contains sufficient accidental impurity to preserve it in the β-phase. This phase is always observed to be heavily twinned and it has been proposed, from transmission electron microscope (TEM) observations of Cr_2O_3 stabilized β-C_2S that the twinning, on (100) planes, occurs to accommodate shear deformations by which the β forms from a higher temperature phase during cooling [7]. The present paper extends the TEM observations of twinning to pure β-C_2S and reports confirmation of their mechanism of formation by hot-stage TEM studies. Observations of the $\beta \rightarrow \gamma$ transformation are also reported and the morphology, orientation and internal structure of γ formed in a β matrix determined by optical microscopy and TEM studies.

2. Experimental procedure

C_2S was produced as follows. Analar calcium

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*The abbreviations usual in cement chemistry are used: $C_2S = 2CaOSiO_2$.

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hydroxide and colloidal silica were mixed in aqueous suspension in a domestic liquidizer. The mixture was then dried and heated to 900° C for one hour to decompose the calcium hydroxide. Pellets of the resultant powder were pressed out at 100 MPa on a hydraulic press and converted to C_2S by heating in air at a temperature of 1390 or 1550° C, for various periods. The initial proportion of $Ca(OH)_2$ and silica were chosen to give a small, 0.1 wt% excess of silica above the stoichiometric composition to provide a trace of liquid at the higher sintering temperature and thereby assist sintering.

Slices of about 30 μm thick of such C_2S as had not dusted were prepared by grinding on SiC papers and examined by transmitted light microscopy.

Subsequently TEM specimens were prepared by ion-beam thinning following standard techniques [8]. The preparation of specimens of β-C_2S which had partially transformed to γ required some patience since fracturing and loss of thin areas sometimes occurred because of the "dusting" effect. Specimens were examined in a 1 MV electron microscope, using a hot stage where appropriate.

3. Results

3.1. The dusting phenomenon

Any specimen of pure C_2S is subject to the risk of dusting on cooling. Dusting was frequently observed, sometimes during cooling and sometimes during subsequent storage of a specimen which had survived the initial cooling. However some specimens survived indefinitely or broke into only a few pieces. Of specimens sintered at 1390° C those sintered for a longer time (1 week) survived better than those heated for a shorter time (1 day). Specimens sintered at 1550° C survived more frequently than those sintered at 1390° C. These results are not in good accord with previous work which has reported less dusting in samples cooled from a lower temperature than from a high one [2]. The present material may differ from that of previous work in being slightly silica-rich. It has been reported that excess silica promotes the $\beta \rightarrow \gamma$ transformation [4]. However a likely explanation of differences between the results of different workers is that material perfection and particularly stresses within the β crystals strongly influence the transformation. Evidence for this is presented below.

Powder X-ray diffraction patterns showed that even specimens which had dusted completely still contained a considerable proportion of untransformed β while intact specimens contained a trace of γ. An intact specimen showed an increase in the proportion of γ after it had been ground up, in agreement with a previous report [9]. The most useful specimens for studying the characteristics of the $\beta \rightarrow \gamma$ transformation were those which had suffered only a small degree of fracturing. Residual pieces of these specimens contained sufficient γ-phase to be readily identified and studied, as described below.

3.2. γ-phase in slightly transformed β specimens

Transmitted light microscopy showed, within grains of the major β-phase, clusters of needle or lath-like particles (Fig. 1). These were determined to be needle or lath-like rather than plate-like by focussing the microscope up and down. They tended to occur in bundles so that the distribution of them was heterogeneous, some grains containing a high density while others were completely free of them. TEM specimens were prepared from such material. By optical examination of the thin areas it could be established where the particles occurred and these areas could then be studied by TEM. Diffraction patterns from such areas showed conclusively that the particles consisted of the γ-phase.

The internal structure of a bundle of γ particles is shown in Figs. 2 and 3. There is an absence of the alternating band constrast typical of the twinned β-C_2S from which the γ must have formed. However, the long axis of the particles appears from optical micrographs to have a unique orientation in a given grain, which coincides with the direction of the boundaries visible in Figs. 2 and 3. By tilting a specimen to obtain two distinct diffraction patterns from the same area of γ it was shown that the unique solution for the crystallographic direction of the particle long axis is [001] (the usual orthorhombic γ cell, $a = 0.509$ nm, $b = 1.14$ nm, $c = 0.678$ nm, is used [3]). It is reasonable to assume that the regions between the boundaries within the areas of γ seen in TEM correspond to the individual particles within the bundles observed optically. These regions are slightly misoriented with respect to one another. For example, diffraction patterns showed the points A and B in Fig. 3 to be misoriented by

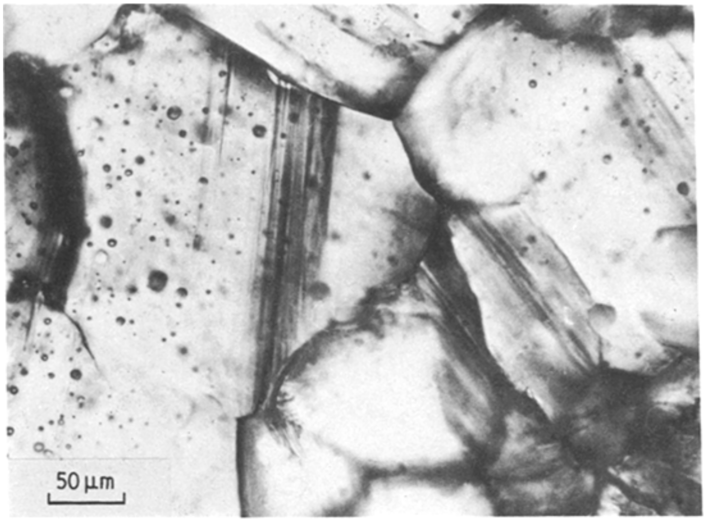

Figure 1 Needles or Laths of γ-C_2S in partially transformed grains of β-C_2S. Transmitted light micrograph of specimen prepared by heating at 1390° C for 1 week.

about 5°, the axis of rotation being neither parallel nor normal to the boundaries. The γ regions contain a fairly high density of dislocations, as seen in Figs. 2 and 3. These often run across the boundaries, confirming that they are of low-angle character. The dislocations, and the low-angle boundaries running parallel to [001], constitute the defect structure visible within γ-C_2S.

Attempts to examine β/γ interfaces have so far been unsuccessful partly perhaps because of mechanical damage in this region arising from the large dilatation accompanying the transformation. Fig. 4 shows γ and twinned β which was nearby. Since the interface was not observable there is a possibility of error, i.e. of the β being in a different domain, but the orientation relationship found, $[001]\gamma$ parallel to $[010]\beta$ is extremely plausible, since the corresponding c and b lattice parameters are very nearly equal, or possibly equal within experimental error (monoclinic β, $a = 0.507$ nm, $b = 0.675$ nm, $c = 0.932$ nm, $\beta = 94.6°$ [10]). Since the $[010]\beta$ axis lies in the $(100)\beta$ twin plane, the orientation relationship $[001]\gamma \| [010]\beta$ can be preserved without the γ acquiring a twinned structure. The apparent parallelism between $(202)\gamma$ in the dark band in Fig. 4 and $(101)\beta$ in the dark twin bands cannot be preserved between the γ and the β from which it originates without the γ developing a twinned structure, which is not observed. The significance of this observation is therefore unclear. Further investigation needs to be made of the β/γ orientation relationship and interface region. The streaking in the diffraction pattern from the γ in Fig. 4 suggests the possibility of faulting parallel to (020). This also requires further investigation. The extra reflections visible in the same diffraction pattern may arise from a small amount of residual β within the γ region. Such extra reflections were not typical and were not seen for example in any of the diffraction patterns taken from the regions of Figs. 2 and 3.

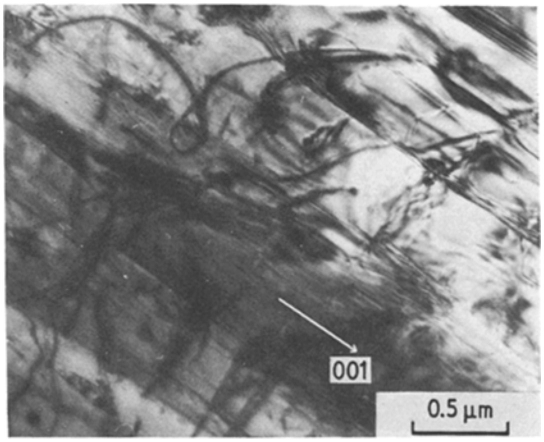

Figure 2 Internal structure of γ-C_2S in partially transformed specimen prepared by heating at 1390° C for 1 week.

3.3. Stress-induced $\beta \rightarrow \gamma$ transformation

It has been reported [9], and confirmed in this work, that further transformation of $\beta \rightarrow \gamma$ can be induced by grinding. This suggests that the transformation can be stress-induced, but does not prove the point since grinding introduces much additional free surface which could of

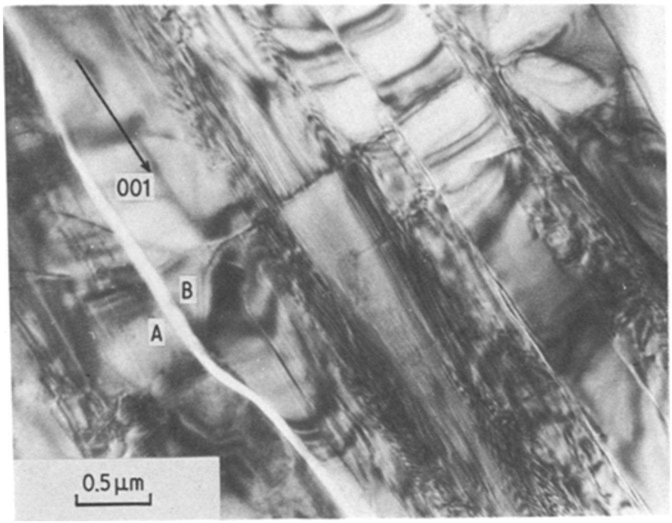

Figure 3 Structure of γ-C_2S – specimen as Fig. 2.

itself be responsible for further transformation. To determine definitely whether the transformation could be stress-induced, microhardness indentations were made on the surface of β-C_2S grains which did not initially contain γ-C_2S. The indentation was carried out on a Reichert microhardness tester at a load of 80 g for a period of 1 min. Fig. 5 shows that γ particles have formed in a position which indicates that tensile stress normal to the long axis of the particle has been effective in inducing the transformation. (The stress distribution round a pyramidal indentation

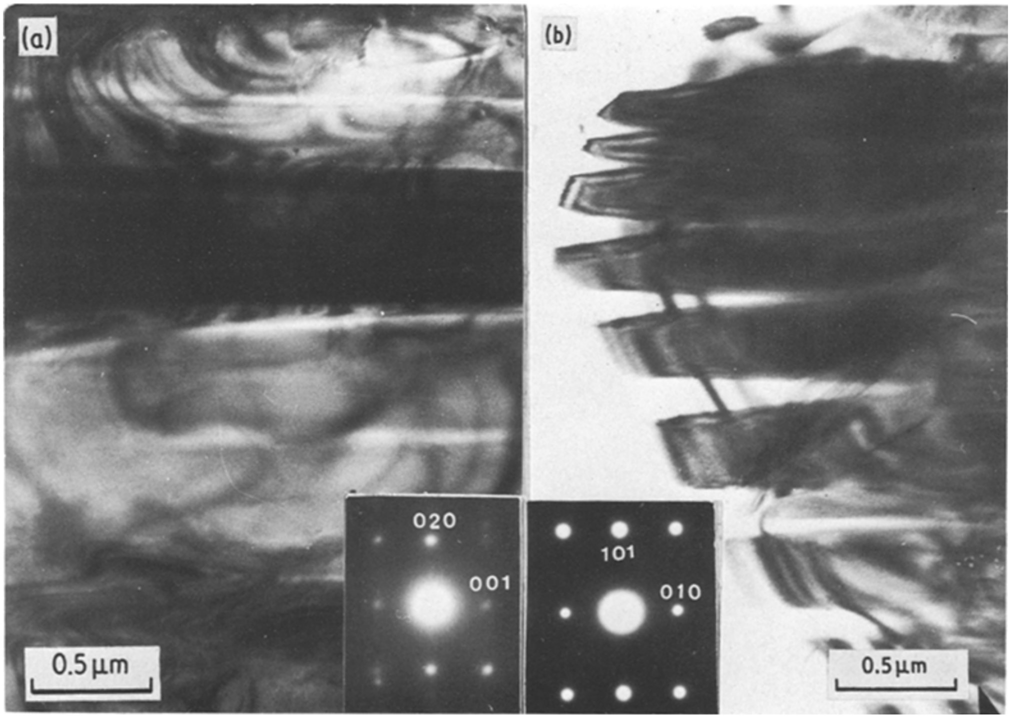

Figure 4 (a) γ-C_2S region with inset diffraction pattern from dark band. (b) Nearby β-C_2S region with inset diffraction pattern from the dark lamellae of the twinned structure. Specimen as for Fig. 2.

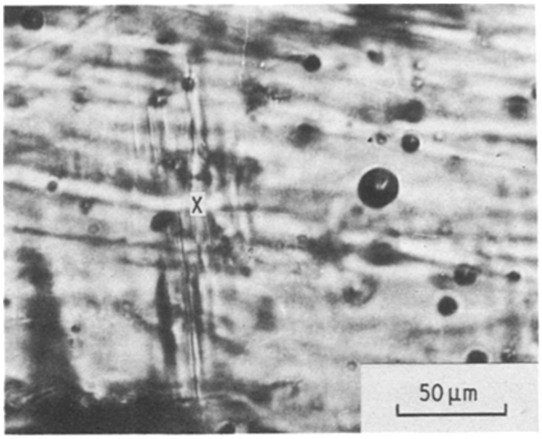

Figure 5 Transmitted light micrograph of specimen prepared as for Fig. 1. Point X is just below the centre of a microhardness indentation, the microscope being focussed just below the surface. The nearly horizontal lines are out-of-focus surface scratches, and the circular markings, pores.

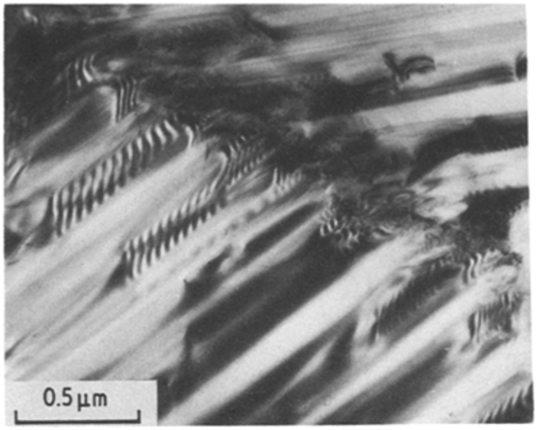

Figure 6 Dislocations at a twin boundary in a C_2S specimen formed by heating at 1550° C for 1 day.

in an anisotropic material is not known, but must qualitatively resemble that around the plastic expansion of a spherical cavity in an ideal plastic solid. This gives a circumferential tensile stress in the plastic zone, rising to a maximum at the elastic/plastic boundary [11]).

3.4. Observations of β-C_2S and the $\beta \rightleftarrows \alpha'$ transformation

Regions of β-C_2S which had not transformed to γ were found to have a similar twinned structure to that previously reported and discussed, in β-C_2S stabilized by 0.5 wt % Cr_2O_3 [7]. There is no evidence that the presence or absence of stabilizing impurity affects the twinning which has been proposed to arise from a lattice shear strain in the α' to β transformation which alternates in sign to reduce long range stress. Dislocations generated at twin boundaries are particularly evident in the pure material; they may move further because of a lower lattice friction stress in pure C_2S than in impure C_2S. An example is shown in Fig. 6. It is proposed that the dislocations move to relax the local stress set up by the lattice transformation shear strain at a domain boundary. The slip plane traces are always parallel to the twin traces, therefore, the slip plane is the same as the twinning plane, identified as $(100)\beta$.

A specimen of pure β-C_2S which had not transformed to γ was heated on a hot stage of the high voltage electron microscope. As the temperature was raised above 750° C twin lamellae started to disappear, but all did not disappear simultaneously. Fig. 7 shows that of the twin lamellae visible at 650° C, all those in one domain and some of those in two others had disappeared at 770° C. (The quoted temperatures should be regarded as accurate in a relative sense but subject to an error of up to about 50° C in an absolute sense, arising from the fact that the hot-stage thermocouple is not in direct contact with the specimen.) This agrees with the previous observation [2] by X-ray techniques of a region of coexistence in practice of β and α' (assuming detwinning to correspond to the $\beta \rightarrow \alpha'$ transformation). At 820° C detwinning was nearly complete and Fig. 8b shows the result of rapid cooling from this temperature. The twins appeared suddenly on cooling. The specimen could be reheated to remove the twins, and it was observed to retwin again on cooling. A slower cooling rate produced wider twins (Fig. 8c). The observations are consistent with the view that the twins develop as a result of a lattice shear strain accompanying the $\alpha' \rightarrow \beta$ transformation and indicate that the reverse transformation $\beta \rightarrow \alpha'$ is accomplished by the reverse shear.

It is noteworthy that transformation of β to γ in the thin section was never observed at any stage of heating or cooling.

4. Discussion

The $\alpha' \rightarrow \beta$ transformation appears to be a relatively straightforward example of a shear transformation in which the required lattice change is very nearly

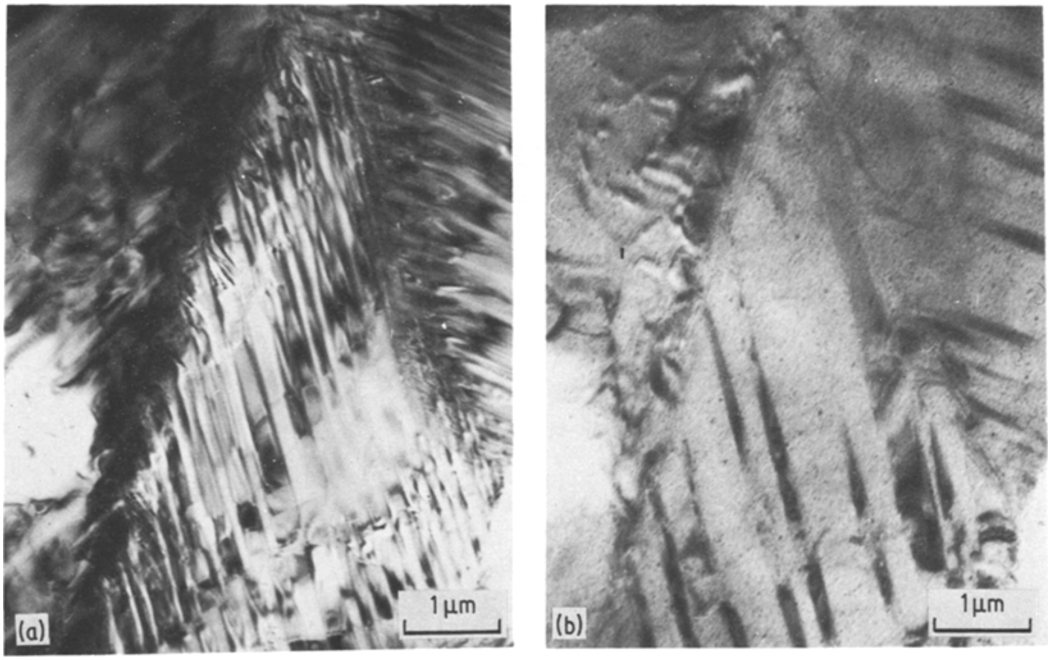

Figure 7 Area of C_2S (a) at 650° C (b) at 750° C (see text for note on accuracy of temperatures). Specimen formed by heating at 1550° C for 1 day, viewed on hot-stage of a high voltage electron microscope.

achieved by a simple shear. There must in addition be a small dilatation, since Klement and Cohen [12] measured a small pressure dependence of the $\alpha' \rightarrow \beta$ transformation temperature, from which they estimated a dilatation of 0.19×10^{-6} m^3 mol^{-1} (about 2.7% of the dilatation accompanying the $\beta \rightarrow \gamma$ transformation). The alternation of the sign of the transformation shear strain to remove long range strains accounts for the twinned structure of the β [7]. Residual short range strains at the termination of twin lamellae are partly relaxed by dislocation glide on (100). In mineralogical terms the transformation is displacive, i.e. primary coordination is not significantly changed [3]. In metallurgical terms the transformation is martensitic, in this case an invariant plane strain being produced by the lattice transformation strain, without the need for an additional lattice invariant shear strain. The great rapidity with which the twins were observed to form on cooling on the hot-stage is consistent with these conclusions. The gap between the temperature of $\beta \rightarrow \alpha'$ and $\alpha' \rightarrow \beta$, and the region of coexistence of α' and β, observed also in previous work [2], argue that there is a nucleation problem for the transformation and its reverse.

The nature of the $\beta \rightarrow \gamma$ transformation is much more problematical. The extremely large dilatation of 14% must have a dominant influence on the transformation. Although the final product is a particle elongated along [001] γ, parallel to [010] β, along which directions there is a very good match of lattice parameters, it is hardly possible for the particle to nucleate as a rod, or any other particle with roughly equiaxed cross-section, in which expansion occurs in all directions normal to the long axis, but not parallel to it. This is because of the very large strain energy requirement of such a morphology. Assuming (in the absence of more detailed information) equal elastic constants for γ and β, and a Poisson's ratio of 0.25, the elastic radial stress σ_r at the interface of cylindrical γ particle can be shown from the appropriate elasticity theory [13] to be

$$\sigma_r = -\frac{2}{3}\mu\frac{\Delta V}{V}$$

where μ is the shear modulus and $\Delta V/V$ the dilatation. This stress amounts to 0.093μ. The tangential stress is equal and opposite, giving a shear stress also of 0.093μ. Such very large stresses could not be supported in the matrix on a macroscopic scale, since they would be relieved by dislocation motion or cracking at physical flaws in the neighbourhood. However in the very small region of perfect crystal surrounding a hypothetical

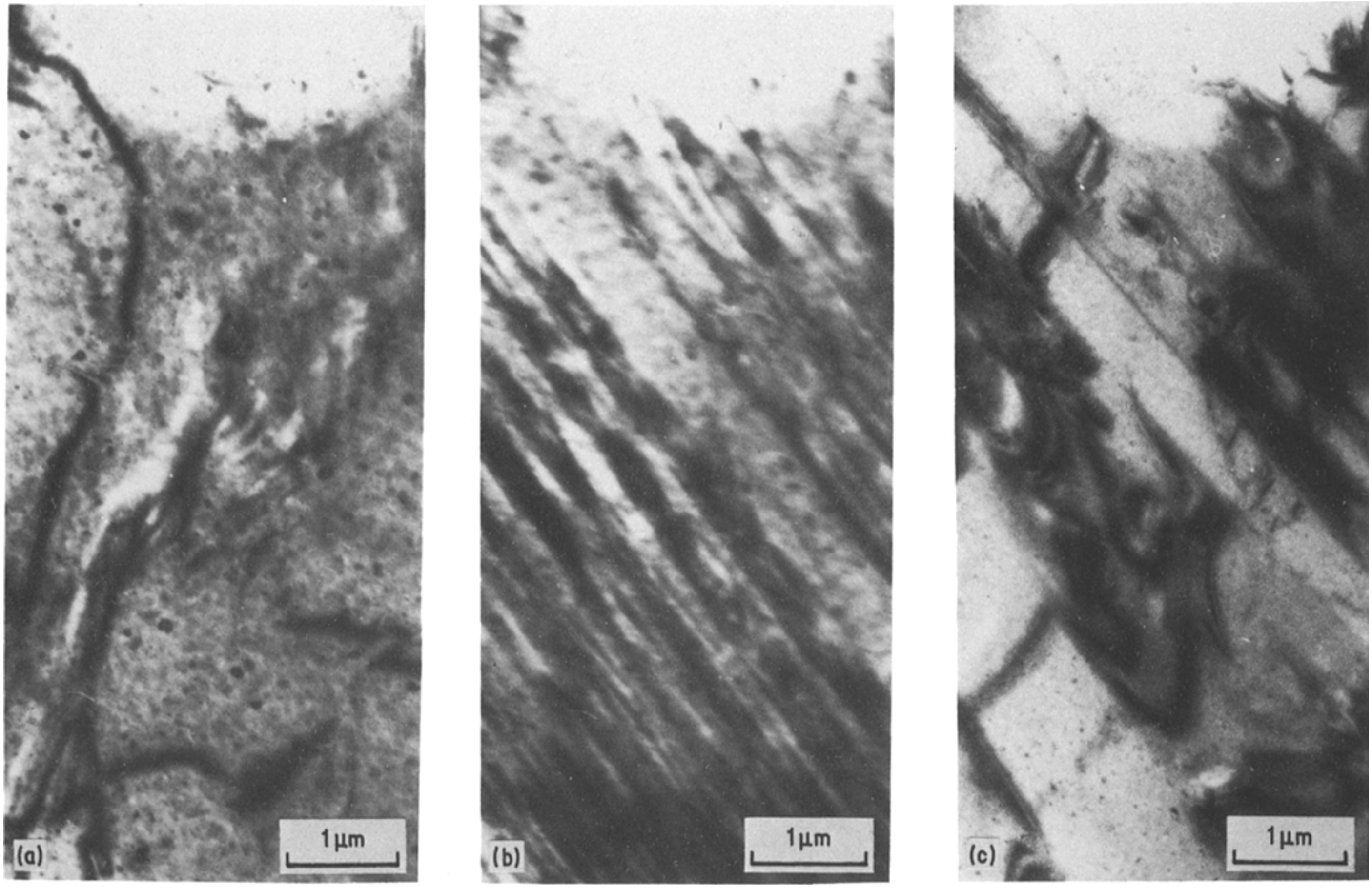

Figure 8 Area of C_2S (a) at 820° C (b) after rapid cooling to room temperature (c) after slower cooling from 770 to 680° C. Same specimen as for Fig. 7.

nucleus such stress might exist. If so, the associated strain energy per unit volume of γ, given simply by

$$E = \frac{1}{2}\sigma_r \frac{\Delta V}{V}$$

would amount to no less than $25.9\,\text{kJ mol}^{-1}$ (taking for μ the value of 80 GPa possessed by forsterite, isostructural with γ-C_2S [14]). This energy would have to be met by the free energy of the $\beta \rightarrow \gamma$ transformation, and this is not possible. The equilibrium temperature at atmospheric pressure of the $\beta \rightarrow \gamma$ transformation lies above the $\beta \rightarrow \alpha'$ transformation temperature; a value of 920° C has been suggested [4]. The enthalpy of the transformation is $-4.9\,\text{kJ mol}^{-1}$ [4], thus, forming the usual linear estimate of the temperature dependence of the free energy of transformation

$$\frac{\mathrm{d}\Delta G}{\mathrm{d}T} \sim \frac{-\Delta H}{T_e}$$

where ΔH is the transformation enthalpy and T_e the equilibrium temperature, we have

$$\frac{\mathrm{d}\Delta G}{\mathrm{d}T} \sim 4.1\,\text{J mol}^{-1}\,\text{K}^{-1}$$

and we see that an impossible supercooling of the order of 6300° C would be required for nucleation in a rod-like morphology. Homogeneous nucleation in rod-like morphology is therefore impossible, and heterogeneous nucleation at sites of internal stress would require assisting stresses to be so high that this also seems unlikely. The more probable form of nucleus would be in the form of a plate with the dilatation concentrated as a strain normal to the faces of the plate, since in this manner the dilatation can be accommodated with less energy [15].

Once a γ particle has grown to a size to bring it close to dislocations and other flaws in the matrix, flow or fracture of the matrix, or both, will restrict the normal stress at the interface and hence reduce the energy requirement for growth to a small fraction of that required for nucleation. Supercooling requirements of only a few hundred degrees may then suffice for the growth of particles even in a needle-like morphology. The perfection of the β matrix will determine the stress which it can support and hence the energy requirement for γ-particle growth. If a relatively defect-free region of β is encountered the energy requirement may rise sufficiently for growth to be halted. This may account for the observation of partially transformed grains of β. The existence of such grains, very evident in Fig. 1, refutes the suggestion [5] that a nucleus, once formed within a β-C_2S grain or particle, will lead to the transformation of the whole grain or particle. This suggestion has been put forward to explain a particle size dependence of the degree of $\beta \rightarrow \gamma$ transformation. There is nevertheless a tendency for the γ particles to occur in bundles and this may be explained by internal stresses, dislocations or microcracking due to the dilatation of one particle assisting in the nucleation and growth of further particles. Such effects are clearly not of themselves sufficient to ensure the complete transformation of a particle or grain, however. The inducement of $\beta \rightarrow \gamma$ transformation by tensile stress normal to $[001]\,\gamma$ is easily understood as the effect of a reduction of the net interfacial normal compressive stress and hence of the strain energy of the transformation. The fact that inducement by a microhardness indentation only occurs in the region of favourably directed tensile stress shows that dislocations, which would be generated all round the indentation, are not of themselves sufficient to induce the transformation. Free surfaces also have no primary role, since transformation was never observed in thin TEM specimens, even when repeatedly heated and cooled. The effect of grinding β-C_2S which has been reported previously [9] and confirmed here must be due to the tensile stresses generated in grinding.

The nature of the $\beta \rightarrow \gamma$ transformation has been discussed in mineralogical terms. Smith *et al.* [3] discusses the relationship between the β and γ structure and point out that there is a reduction in coordination of some calcium atoms in changing from β to γ and that rotation of SiO_4 tetrahedra is required, but that there are some similarities in the arrangements of atoms. They term the transformation "semi-reconstructive". Whether the transformation is martensitic in character is less easy to decide. The critical question of whether a shape change (other than dilatation) accompanies the transformation is undetermined. Martensites normally have a plate morphology with the plane of the plate an invariant plane of the shape change, and frequently have an internally twinned structure arising from a combination of twinning with the lattice transformation strain to produce the invariant plane strain. Neither of these characteristics are shown by the $\beta \rightarrow \gamma$ transformation. Lath martensite does however occur in low carbon steels [16]. The reason for a lath as opposed to plate morphology in this case is not understood, although other features of the transformation have been explained [17]. The fact that the $\beta \rightarrow \gamma$ transformation occurs isothermally does not conclusively rule out a martensitic character since isothermal martensite is known, although an athermal transformation is more characteristic [18]. Perhaps the most compelling argument against a martensitic mode of propagation for the transformation comes from a comparison of the twinned β structure and the untwinned γ structure. In the theory of a martensitic transformation a habit plane (the invariant plane) would be predicted and unless this coincided with the (100) twin plane of β, or a plane normal to (100), it would not be continuous across twin boundaries. The prediction of habit plane follows from a choice of lattice correspondence and mode of lattice invariant shear strain required to produce an invariant plane. Apart from the correspondence between [001] γ and [010] β (equal lattice spacings) the choice of these elements is not obvious but it is unlikely that any reasonable choice would lead to a habit plane and orientation for the γ which were continuous across the twinned structure.

The fact that the transformation can be stress-induced does not relate directly to the question of martensitic character. It is interesting to speculate upon the possible induction of the transformation by the tensile stresses acting near the tip of a crack. Stress-induced phase transformation at crack tips in zirconia-containing ceramics has led to considerable toughening of the material [19]. The dilatation in the $\beta \rightarrow \gamma$-C_2S transformation is 2.6 times greater than that in the (martensitic) zirconia transformation, suggesting the possibility of a toughening effect in suitable systems incorporating unstabilized β-C_2S.

5. Conclusions

1. The $\alpha' \rightarrow \beta$ transformation in C_2S occurs by a reversible shear mechanism in which alternation of the sign of the shear leads to (100) twinning. The shear displacements at the boundaries of twinned domains are accommodated by (100) slip.

2. The $\beta \rightarrow \gamma$ transformation in C_2S occurs by the growth of needles or laths whose long axes are parallel to [001] γ and [010] β. The particles tend to occur in clusters but individual grains of β are frequently incompletely transformed.

3. The interior of regions of γ contains a high density of dislocations and of low boundaries running parallel to the long axis. The γ is not internally twinned.

4. The growth of γ is unlikely to be martensitic in character.

5. The $\beta \rightarrow \gamma$ transformation can be induced at room temperature by local tensile stresses normal to the long axis of the needles or laths.

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