T.e.m. Studies of Cement Clinker Compounds, their Hydration and Strong Cement Pastes [and Discussion]

G. W. Groves, J. P. Skalny, L. J. Parrott and K. Kendall

| **Email alerting service** | Receive free email alerts when new articles cite this article - sign up in the box at the top right-hand corner of the article or click **here** |

T.e.m. studies of cement clinker compounds, their hydration and strong cement pastes

By G. W. Groves

Department of Metallurgy and Science of Materials, University of Oxford,
Parks Road, Oxford, OX1 3PH, England, U.K.

[Plates 1 and 2]

Ion-beam thinned specimens of cement-forming compounds and cement pastes have been examined by transmission electron microscopy (t.e.m.). The triclinic lattice of pure tricalcium silicate has been confirmed and twins corresponding to domains of the superlattice have been observed. Thinned specimens of tricalcium aluminate show a copious amorphous reaction product at the surface after dipping into alkaline calcium sulphate solution, confirming the mechanism of retardation by blocking access to the surface. Observations of tricalcium silicate after it has been dipped into solution in contact with hydrating tricalcium silicate both with and without calcium chloride suggest that calcium chloride additive may accelerate hydration by improving access to the surface. Cement pastes of high strength ('macro-defect-free' pastes) show a similar fine-scale microstructure to cement pastes of low water content made by conventional techniques.

1. Introduction

A number of observations, by transmission electron microscopy (t.e.m.), of ion-beam thinned specimens of cement clinkers, cement forming compounds and cement pastes have recently been reported. Jennings *et al.* (1981) and Dalgleish *et al.* (1980) studied pastes of tricalcium silicate (C_3S) of various ages, including quite young pastes reinforced by resin for the purpose of thinning, and identified different forms of hydration product. Groves (1981 a) made a study of the microstructures of the major phases of ordinary Portland cement clinker and reported on the nature and origin of twinning in β-dicalcium silicate (βC_2S) (Groves 1982). Hudson & Groves (1981) examined the alite (impure C_3S) phase in ordinary Portland cement clinkers and showed that the majority of alite had the monoclinic structure determined by Jeffery (1952), and was twinned.

In the present study a variety of new observations are reported. Pure C_3S and tricalcium aluminate (C_3A) have now been examined and early stages of their hydration in water and other solutions have been studied by immersing a thinned specimen for a fixed period and then observing it by t.e.m. after withdrawal from solution. Cement pastes of low water/cement ratio (w/c) are particularly suitable for ion-beam thinning because of their relatively high strength. The microstructure of the recently developed 'macro-defect-free' (MDF) cement pastes has been compared with that of other ordinary pastes of low water content.

2. Results and discussion

(a) *The lattice and microstructure of pure tricalcium silicate* (C_3S)

An examination was made of pure C_3S in the form of flux-grown crystals kindly supplied by the National Bureau of Standards, Washington D.C., and also in the form of sintered specimens prepared in our own laboratory. Specimens were ion-beam thinned by standard techniques. Both materials showed the same electron diffraction patterns, which were quite distinct from patterns obtained from alites (impure C_3S) in cement clinker (Hudson & Groves, 1981). A prominent pattern is shown in figure 1, plate 1. From this and two other patterns from different orientations the reciprocal lattice was deduced and inverted to form the true direct lattice. This lattice was in complete agreement with that reported by Golovastikov *et al.* (1975), which was based on X-ray rotation photographs of single crystals. The lattice is triclinic, $a = 1.167$ nm, $b = 1.424$ nm, $c = 1.372$ nm, $\alpha = 105°\ 30'$, $\beta = 94°\ 20'$, $\gamma = 90°$. Lattices suggested in earlier work on the basis of X-ray powder photography (as listed, for example, in Taylor 1964) were found to be inapplicable, except with regard to the pseudolattice. The same pseudolattice, nearly trigonal, $c = 2.5$ nm, $a = 0.7$ nm, occurs for all forms of C_3S, including alites. The strong pseudolattice reflexions can be easily picked out in figure 1, and two of them are indexed on the plate. The remaining reflexions, which may be termed superlattice reflexions are relatively weak although they approach the pseudolattice reflexions in intensity as the specimen thickness increases. The ease with which even very weak superlattice reflexions are observed in t.e.m. is a great advantage in identifying the true lattice. Pure C_3S contains reflexion twins on the mirror planes of the pseudolattice, $\{2\bar{1}\bar{1}0\}$, which may be considered as domains in an originally trigonal structure, within which different but equivalent orientations are chosen for the superlattice planes. An example of this type of twinning is shown in figure 2. The weakness of the contrast between the twins is presumably a result of their giving the same strong pseudolattice reflexions, as can be seen in the diffraction patterns shown in the plate. These twins are exactly similar in character to those reported in alite, which has a quite different superlattice but the same pseudolattice as pure C_3S (Hudson & Groves 1981).

(b) *Early hydration of tricalcium aluminate* (C_3A)

The hydration products formed at the surface of thinned pure C_3A specimens, after dipping the specimen for a short time in water and in a solution co-saturated with calcium sulphate and calcium hydroxide, were compared. After immersion in water for 5 min the specimen, when removed from the water and allowed to dry, appeared to be remarkably clean with perhaps a trace of product at the edge. No diffuse diffraction ring or reflexions other than those of pure C_3A could be detected in diffraction patterns taken from regions at the specimen edge. The alkaline calcium sulphate solution, which was meant to simulate approximately the environment of C_3A in a Portland cement (retarded with calcium sulphate) shortly after the addition of water, produced a copious reaction product, after a similar 5 min immersion period. The product obscured the edge of the specimen completely (figure 3). In agreement with the findings of Bailey & Chescoe (1980), the reaction product appears from diffraction patterns to be completely amorphous, in spite of its somewhat fibrous morphology. The observations support the view, which is now becoming widely accepted, that the calcium sulphate acts as a retarder for the hydration of C_3A by very quickly (within *ca.* 5 min) smothering its surface with reaction products.
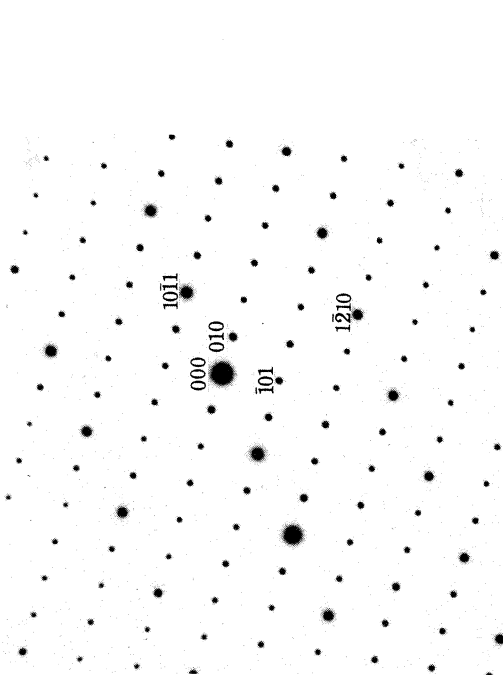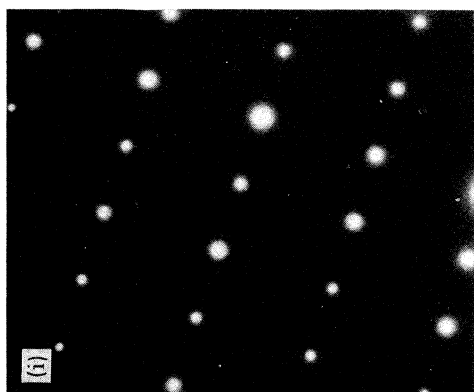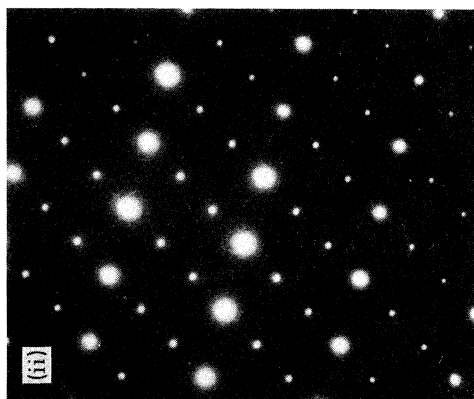
FIGURE 1. Electron diffraction pattern of a pure tricalcium silicate crystal.
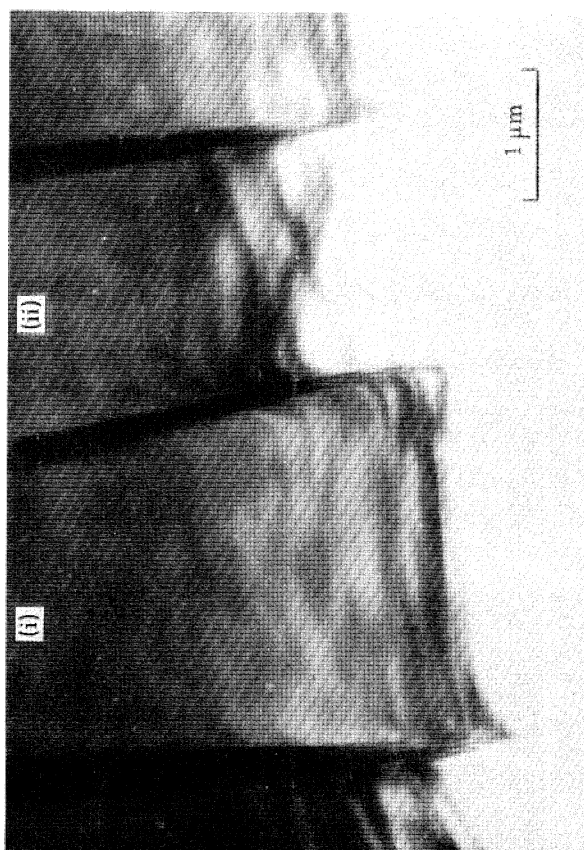

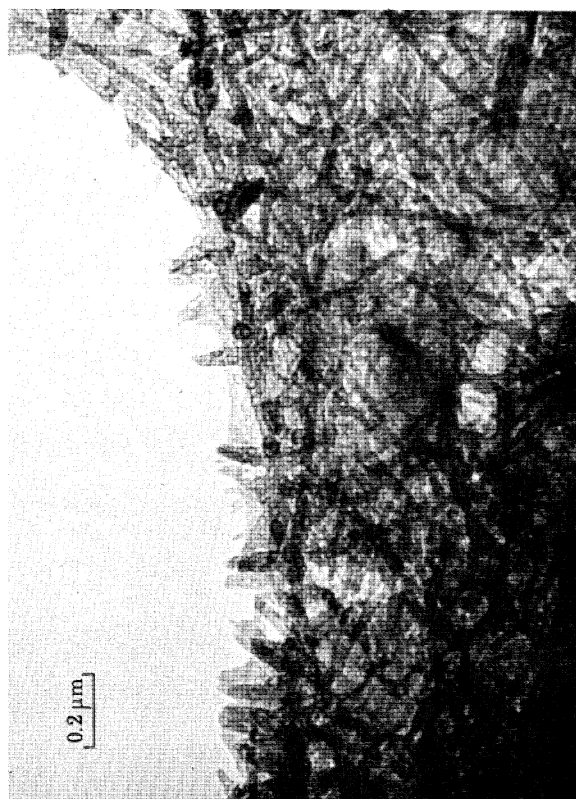FIGURE 2. Twins in pure tricalcium silicate, with electron diffraction patterns from the regions (i) and (ii).

FIGURE 3. Amorphous surface coating formed on tricalcium aluminate immersed in alkaline calcium sulphate solution for 5 min.
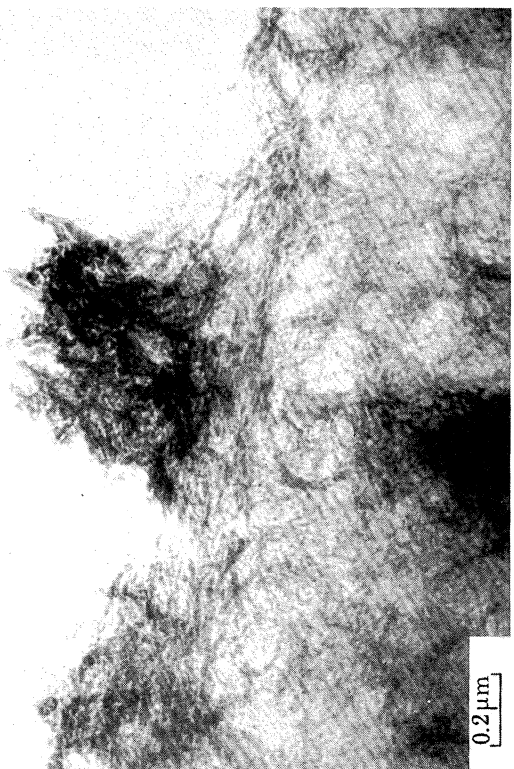
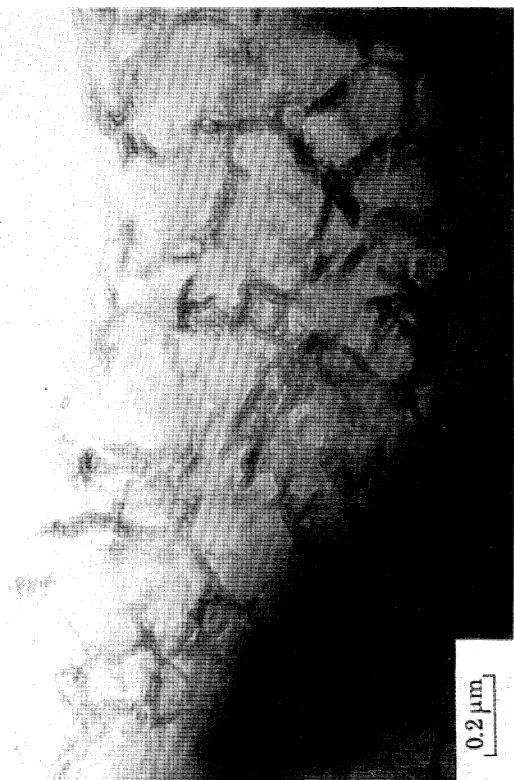FIGURE 5. Edge of a tricalcium silicate specimen after immersion in calcium chloride solution for 3 h.

0.2 μm

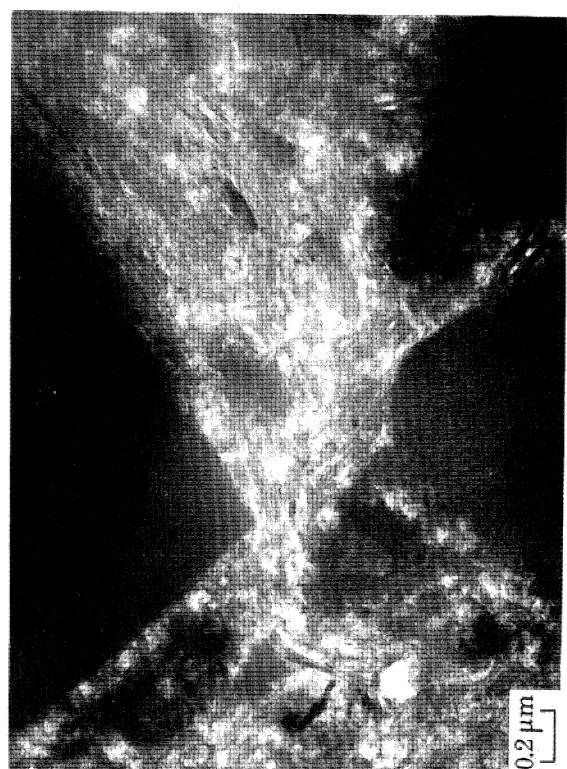FIGURE 7. Lamellae of calcium hydroxide embedded in hydrate gel in a macro-defect-free cement paste.

0.1 μm

FIGURE 4. Edge of a tricalcium silicate specimen after immersion in water for 3 h.

0.2 μm

FIGURE 6. Macro-defect-free cement paste microstructure. The large dark regions are residual cement clinker.

0.2 μm

(c) Early hydration of pure C_3S

Thinned specimens were examined after immersions of 3 h and 6 h in the supernatant liquid of a $2:1$ w/c ratio paste made with pure C_3S powder, the paste being mixed immediately before the immersion. After immersion the specimens were rinsed in water, drained and allowed to dry. For comparison, specimens were immersed for the same times in the liquid of a similar paste made with a 2 % solution of the accelerator calcium chloride.

After 3 h in water a quite copious reaction product could be seen (figure 4, plate 2). Diffraction patterns normally showed both sharp reflexions and a diffuse ring, indicating amorphous material lying on crystalline C_3S, but an aperture selecting only the regions within $ca.$ 0.3 μm of the edge produced only the diffuse ring pattern indicating an amorphous coating standing out from the edge. After 6 h immersion in water a very prominent amorphous zone $ca.$ 1 μm in width was visible at the edge of the specimen. An immersion of 3 h in the accelerated cement solution left some amorphous material on the specimen surface (figure 5) but it appeared to be less copious than it was after immersion in the non-accelerated solution. After 6 h the microporous regions visible in figure 5 had spread to cover the surface but it was not possible to obtain a diffraction pattern from the extreme edge showing only a diffuse ring. Crystalline reflexions were always visible in addition to the diffuse ring. This indicated that there was not a coating standing out from the edge.

Although many further experiments need to be performed to establish the consistency of these observations, the preliminary results lead to the tentative suggestion that the role of calcium chloride in accelerating the hydration of C_3S may be approximately the reverse of the role of calcium sulphate in retarding the hydration of C_3A, i.e. that it acts by increasing the accessibility of the surface to hydration. Exactly how this comes about is not yet clear.

(d) Microstructure of strong pastes

The detailed microstructure of pastes made with the addition of a water-soluble polymer and processed to give MDF cement appears to be indistinguishable from that of other pastes made with a low water content, but not using water-soluble polymer. All the pastes examined have been relatively young – typically about one month old – and contain large amounts of un-hydrated clinker, which unfortunately thins more slowly under the ion beam than the hydration products. This leads to a specimen of very irregular thickness, and it is a great advantage to examine such specimens under a 1 MV electron microscope, with its ability to penetrate thicker regions of the specimen.

A typical region of a MDF paste is shown in figure 6. This paste was mixed with water-soluble polymer and passed between rollers, following the type of process described in I.C.I. patents (Birchall *et al.* 1983). It was then hydrated for 4 weeks at 50 °C and because of the elevated temperature of hydration is probably more hydrated than is usual for MDF paste although there was no striking difference in microstructure between this paste and one hydrated at room temperature. A prominent feature of the microstructure is the presence of a dense homogeneous region of amorphous gel round the edge of clinker grains. Such regions have been seen in other pastes, for example C_3S pastes made in the normal way (Jennings *et al.* 1981), so they are clearly not a special feature of MDF pastes. Outside these regions the hydration product is an intimate mixture of crystalline and amorphous material. Diffraction from a region of 1 μm diameter in this outer hydration product nearly always shows a diffuse ring together with some crystalline

reflexions, and regions showing diffraction contrast within the outer hydration product can usually be detected by tilting the specimen. One source of crystalline material is calcium hydroxide, which is present in a microcrystalline form (Groves 1981 b). This consists of groups of very thin lamellar crystals, the plane of the lamellae being parallel to the basal plane (0001) of calcium hydroxide. The lamellae tend to lie approximately parallel to one another but are not otherwise oriented with respect to one another. A very small group of calcium hydroxide microcrystals is shown in figure 7, taken from the same cement as figure 6. Again, microcrystalline calcium hydroxide is not a special feature of MDF pastes but is detectable in other pastes of low water content.

3. Conclusions

(a) Electron diffraction patterns confirm that the lattice of pure C_3S is that found by Golovastikov et al. (1975). Twins are observed that can be regarded as domains of different superlattice orientation within the trigonal pseudolattice.

(b) Observations of thinned specimens after they had been dipped into appropriate solutions confirm that calcium sulphate retards the hydration of C_3A by forming a copious amorphous reaction product at its surface, and suggest that calcium chloride may accelerate the hydration of C_3S by reducing the amount of reaction product adhering to the surface.

(c) Observations of MDF cement pastes show that their fine-scale microstructure is similar to that of other cement pastes of low water content made in a conventional way. This is consistent with the view that the relatively high strength of MDF pastes is due to the absence of the larger pores present in conventional pastes (Birchall et al. 1983).

References

Bailey, J. E. & Chescoe, D. 1980 In *Proc. 7th Int. Congr. Chem. Cem., Paris*, vol. 4, p. 595.
Birchall, J. D., Howard, A. J. & Kendall, K. 1983 *Metallurgist. Mater. Technol.* **15**, 35.
Dalgleish, B. J., Pratt, P. L. & Moss, R. J. 1980 *Cem. Concr. Res.* **10**, 665.
Golovastikov, N. I., Matveeva, R. G. & Belov, N. V. 1975 *Kristallografiya* **20**, 721.
Groves, G. W. 1981a *J. Mater. Sci.* **16**, 1063.
Groves, G. W. 1981b *Cem. Concr. Res.* **11**, 713.
Groves, G. W. 1982 *Cem. Concr. Res.* **12**, 619.
Hudson, K. E. & Groves, G. W. 1981 *Cem. Concr. Res.* **12**, 61.
Jeffery, J. W. 1952 *Acta Crystallogr.* **5**, 26.
Jennings, H. M., Dalgleish, B. J. & Pratt, P. L. 1981 *J. Am. ceram. Soc.* **64**, 567.
Taylor, H. F. W. 1964 In *The chemistry of cements* vol. 2, p. 367. London: Academic Press.

Discussion

J. P. SKALNY (*Martin Marietta, Baltimore, U.S.A.*). First, is it possible that the differences in the morphology of C_3S with or without calcium chloride are due to different rates of C_3S hydration, resulting in different morphologies at equal time (three hours)? Second, is the observed 'porosity' due to damage by the electron beam?

G. W. GROVES. Three hours with calcium chloride is equivalent to about six hours without and there is a marked difference between the morphologies after three hours with calcium chloride and six hours without. In answer to the second question, from my experience, no.

L. J. PARROTT (*Cement and Concrete Association, Slough, U.K.*). Was the crack, shown in Dr Groves's micrograph of water hydrated tricalcium silicate, due to drying shrinkage of the calcium silicate gel?

G. W. GROVES. This is perfectly possible.

K. KENDALL (*I.C.I. New Science Group, Runcorn, Cheshire, U.K.*). Dr Groves showed electron micrographs of thinned samples of cement clinker that had been dipped in water and became covered with a layer of gelatinous material. Is this gelatinous layer the elusive membrane referred to by Dr Double in his paper? If so, is there any electron microscope evidence that the gel layer is disrupted by an osmotic pumping mechanism as suggested by the membrane model of cement hydration?

G. W. GROVES. The answer to the first question is that I do not know and the answer to the second question is no.
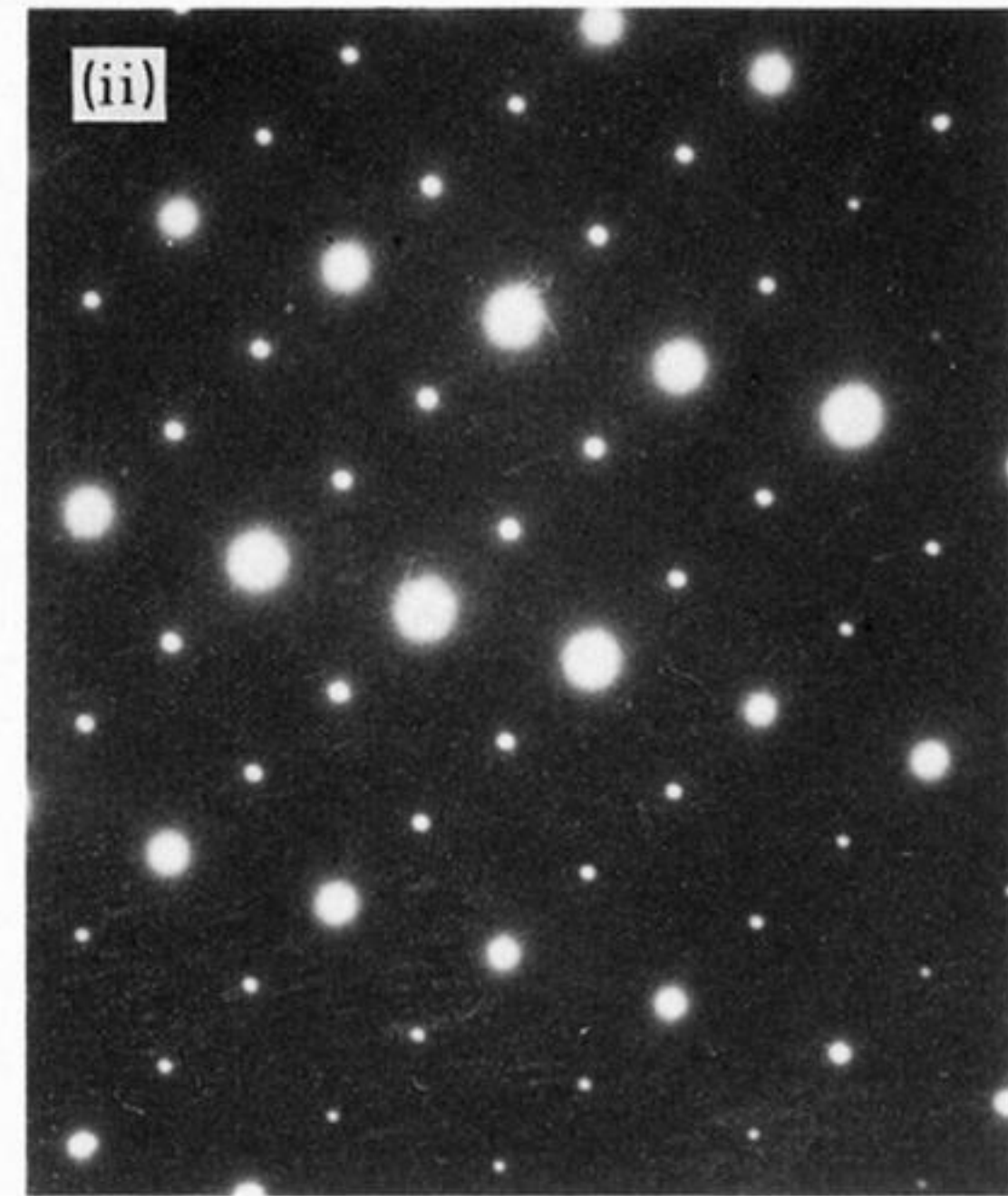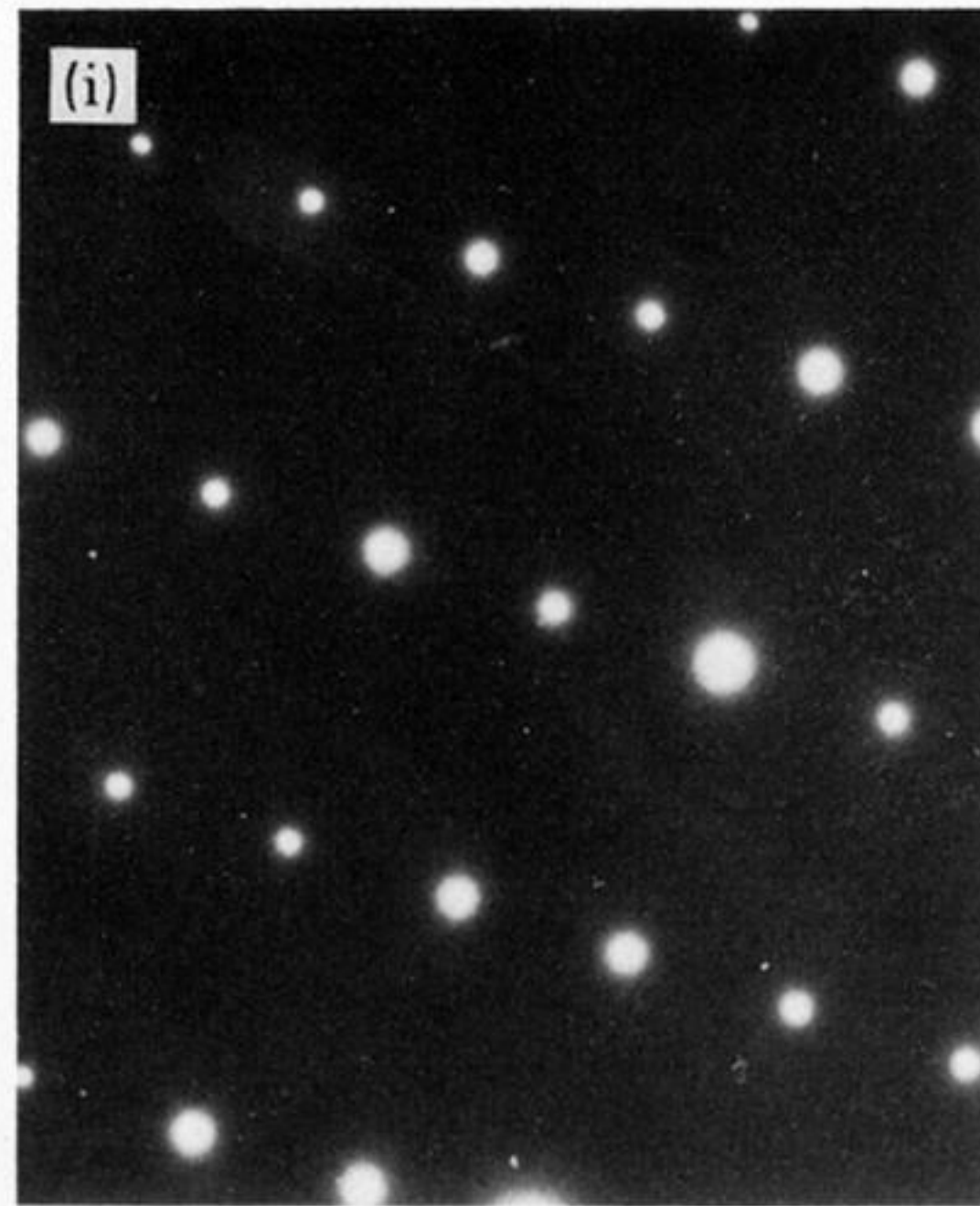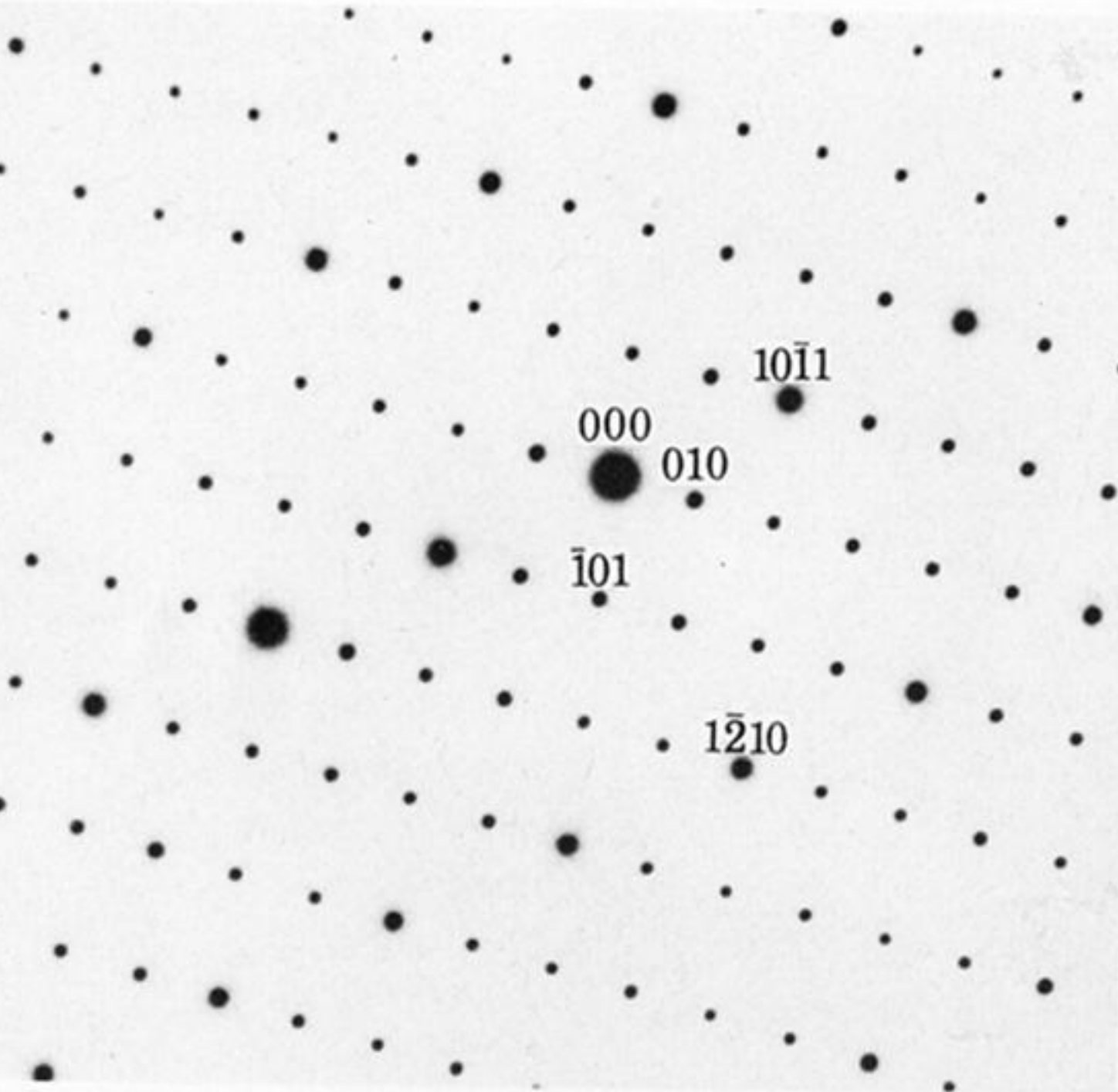
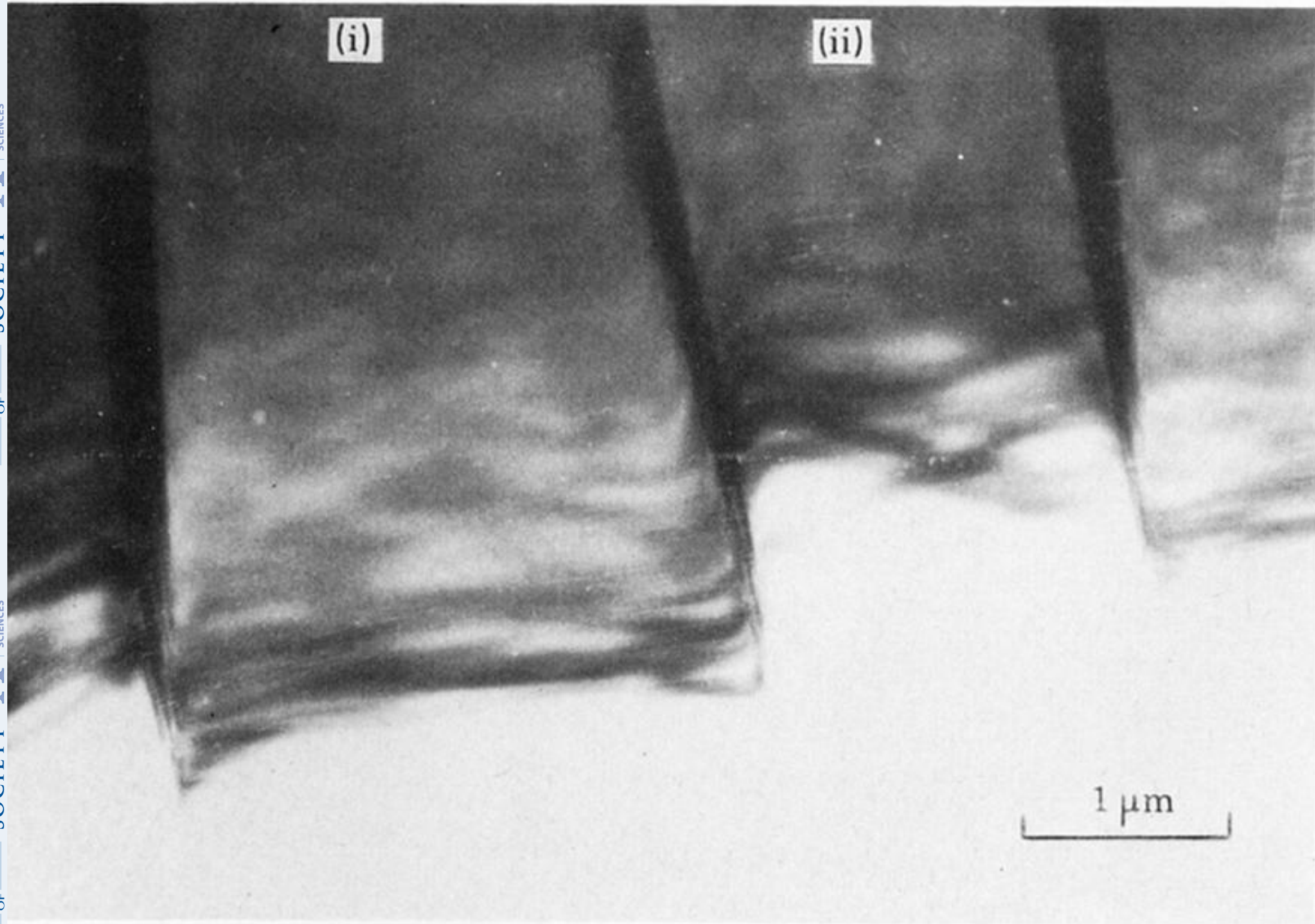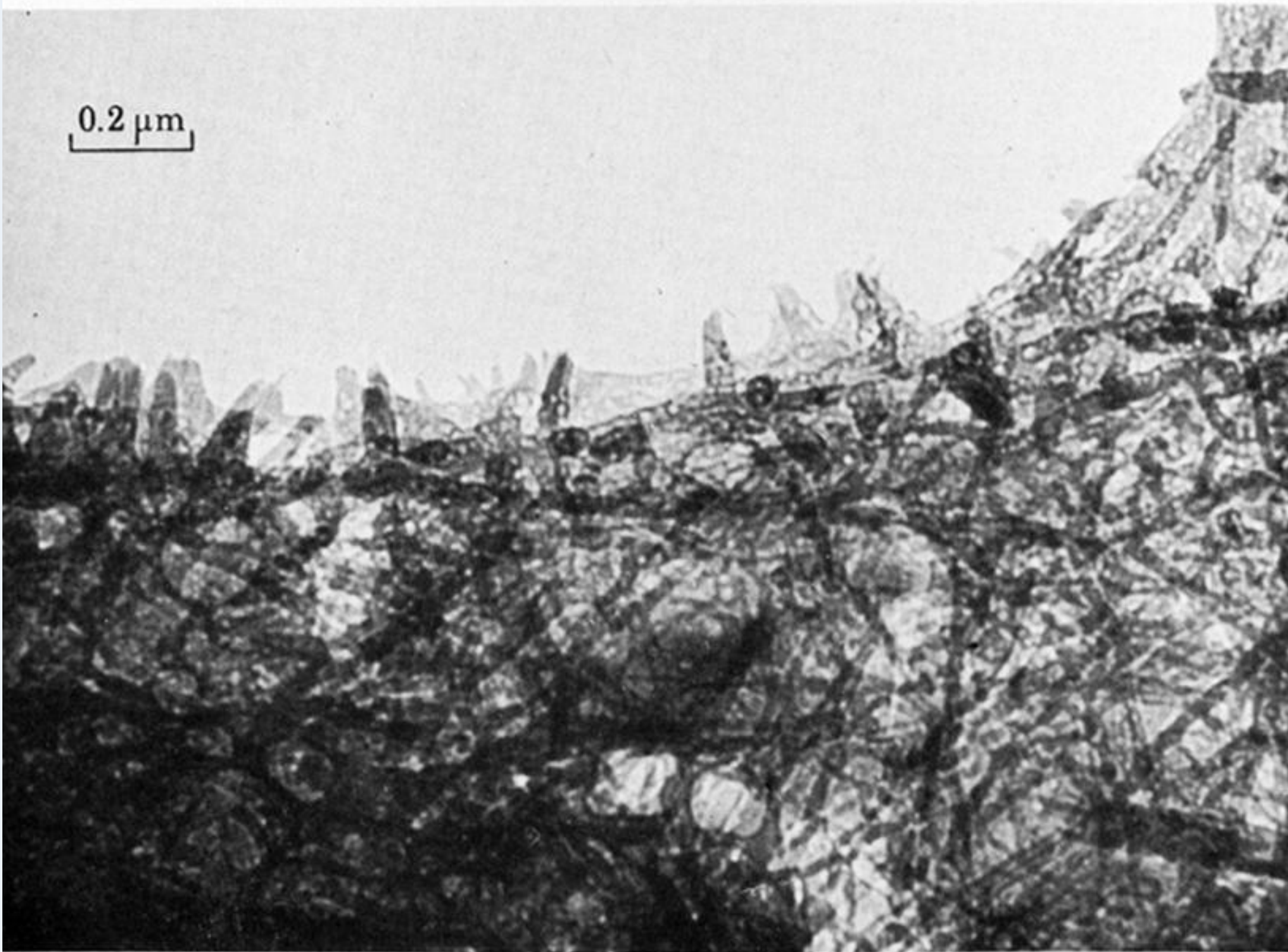FIGURE 1. Electron diffraction pattern of a pure
tricalcium silicate crystal.

FIGURE 2. Twins in pure tricalcium silicate, with electron diffraction patterns from the regions (i) and (ii).

FIGURE 3. Amorphous surface coating formed on tricalcium aluminate immersed in alkaline calcium sulphate solution for 5 min.
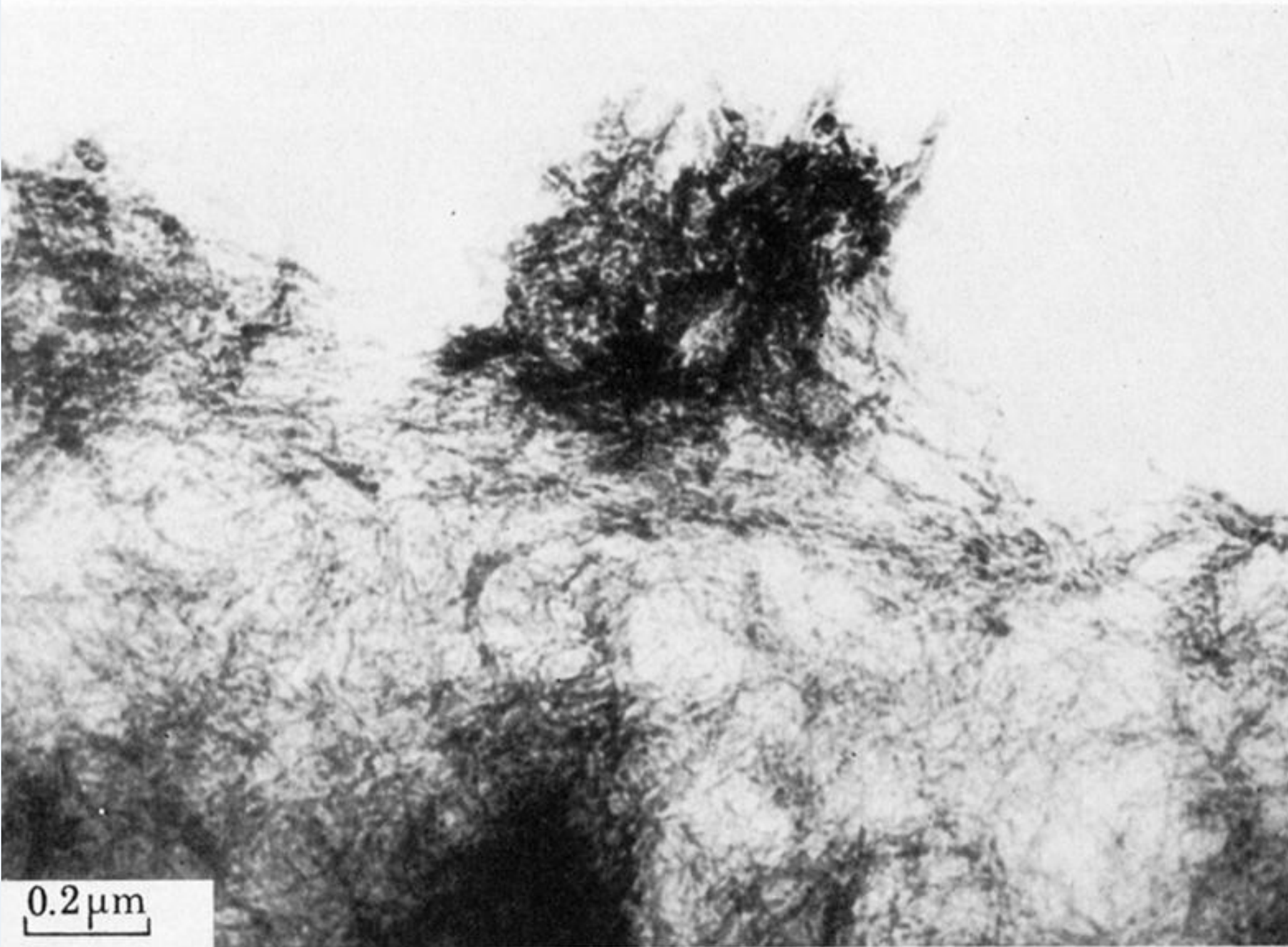
0.2 μm

FIGURE 4. Edge of a tricalcium silicate specimen after
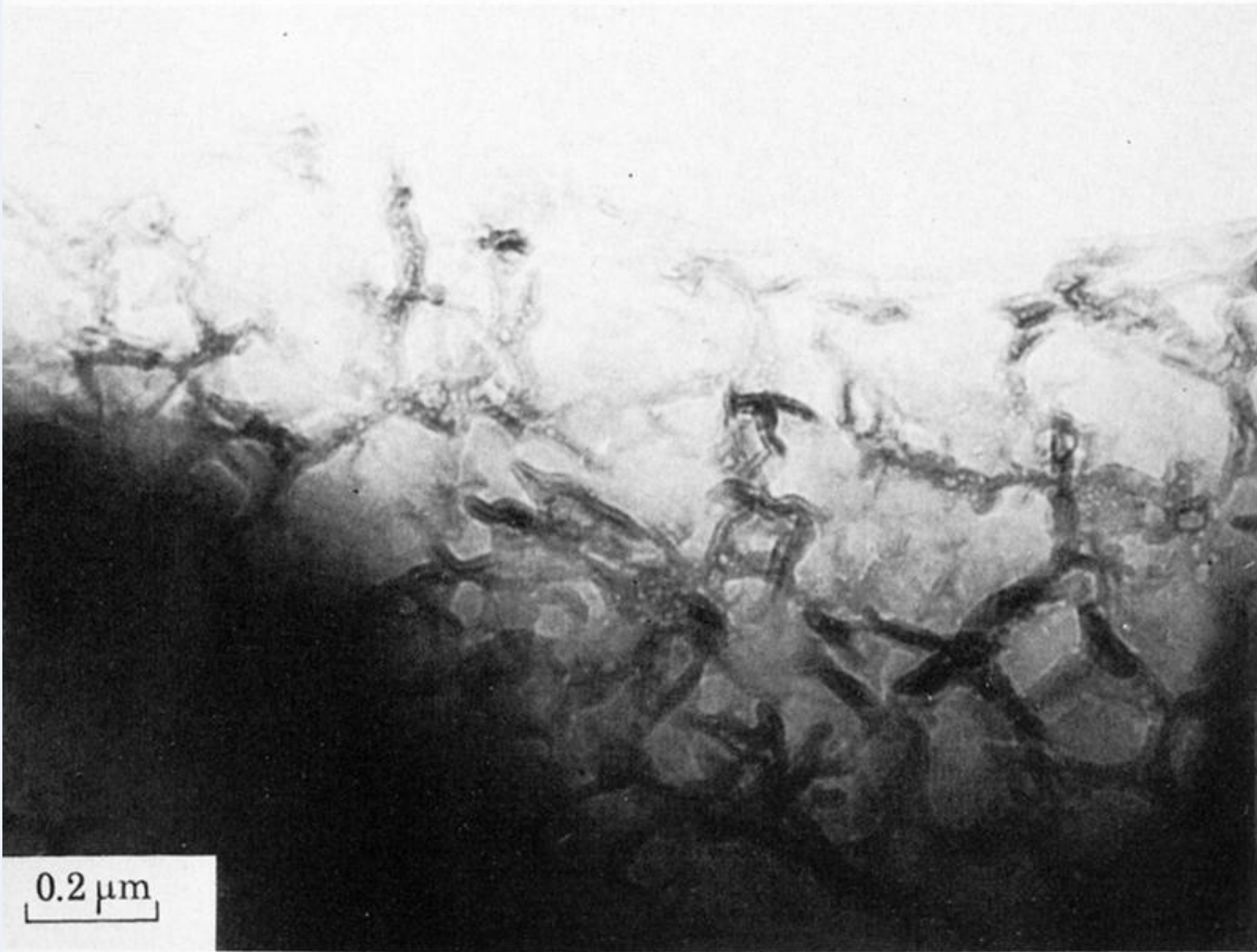immersion in water for 3 h.

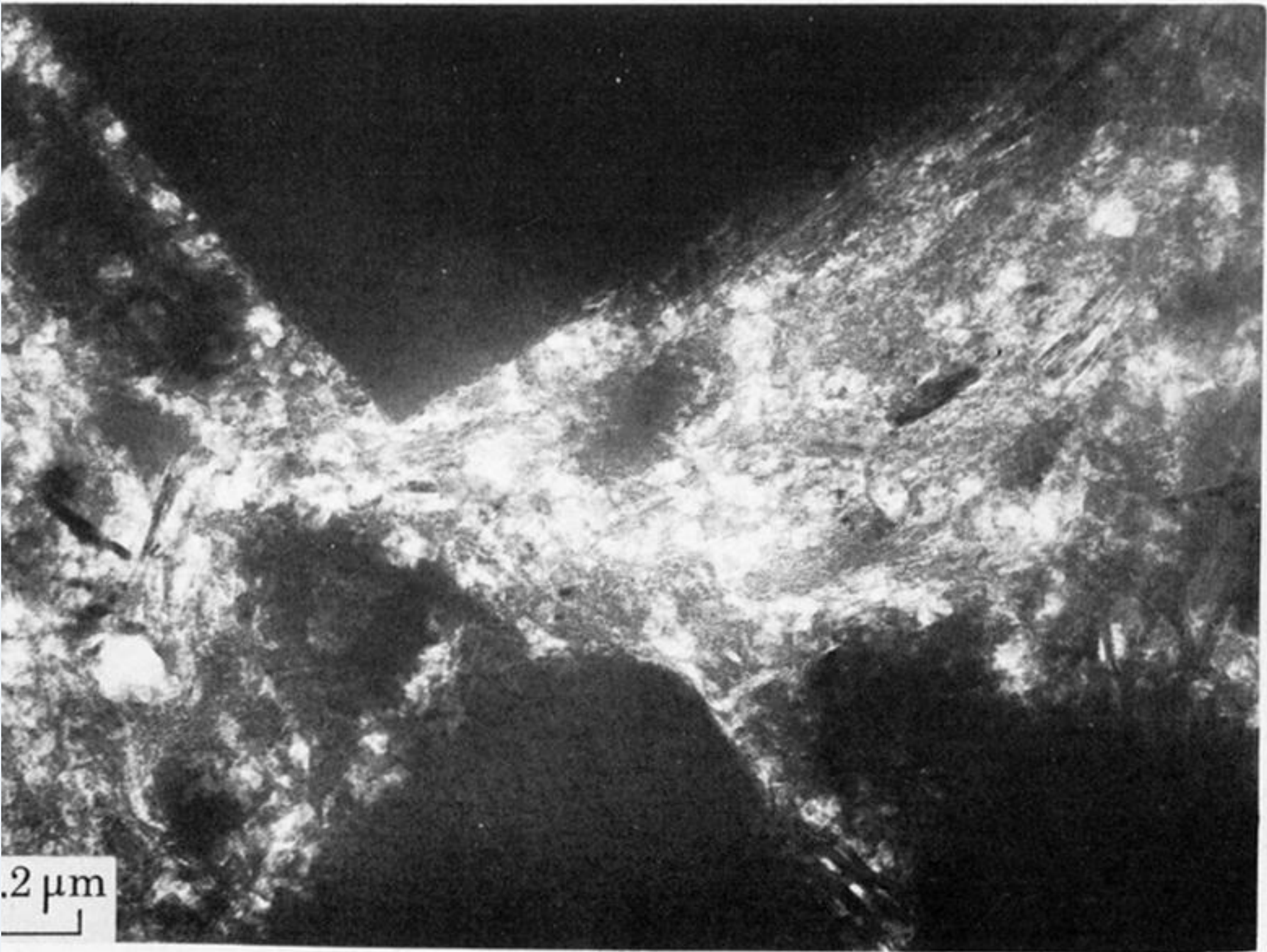FIGURE 5. Edge of a tricalcium silicate specimen after immersion in calcium chloride solution for 3 h.

FIGURE 6. Macro-defect-free cement paste microstructure. The large dark regions are residual cement clinker.

FIGURE 7. Lamellae of calcium hydroxide embedded in hydrate gel in a macro-defect-free cement paste.