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# Ion beam etching in the study of cementitious materials

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## 1. Introduction

The usefulness of electron microscopy and diffraction in the study of cementitious material is an accepted point of view [1, 2]; of particular interest is the morphology and composition data that can be acquired using an energy dispersive X-ray detection system (EDS) coupled to the scanning electron microscope (SEM) [3, 4]. Ion etching/thinning techniques have been used as an adjunct to this combination, and it has been found that with proper use they can improve the recognition and study of features such as phase delineation and composition, defects, cracks and pores. The technique can also introduce undesirable artifacts, and so part of this work has been aimed at elucidating the optimum conditions for its use. The general applicability of ion-etching and its limitations of use with cementitious material are discussed; the study has been mainly confined to unhydrated cement clinker sections, though some results with stress-fractured rock are also reported.

## 2. The problem

With X-ray fluorescence microprobe analysis the main requirements for *accurate* analysis are ease and speed of phase recognition and the presentation of smooth, flat, clean specimen surfaces for study [5]. A number of well-known techniques do exist for the delineation of cement phases but possess some incompatibility with the requirement of smooth, clean surfaces. The conventional secondary electron SEM image is generally not clear as far as cement grain differentiation is concerned. Yet speed of phase recognition and subsequent location of the electron microprobe is important since unavoidable medium term (about 5 min, say, for a Cambridge Stereoscan Mark II) fluctuations in the electron beam intensity during analysis work seriously degrades the accuracy of the analysis. Such SEM beam variations may be unimportant for imaging purposes but cannot be ignored in microanalysis work. Continual restandardization of electron-optical conditions would go part of the way in arresting this degradation, but would be very tedious and would greatly increase the average total time for analysis. Flat, smooth specimen surfaces of accurately known tilt angle are required for accurate X-ray absorption corrections. The necessity for clean surfaces is self-evident.

Two popular techniques of phase delineation – chemical etching and X-ray mapping – work well but suffer a number of drawbacks. For example, chemical etching with various reagents, often used in optical studies, suffers from galvanic action, reaction product deposition and leaching of the clinker surface. On the other hand, X-ray mapping, while being a clean, non-destructive method yielding clear, unambiguous phase delineation [6], has but one important disadvantage in that it is a relatively slow method (300 to 600 sec are typical counting times for useful elemental maps based on the silicon $K\alpha$ transition).

In contrast, ion-beam etching is generally a "clean" method (some metallic sputtering from the source aperture is possible), though not always characterized and so it has been investigated in connection with cementitious surfaces as an aid to SEM/EDS microanalysis and other electron microscope studies. The experimental arrangement used is now discussed.

## 3. Ion beam etching

Ion beam etching is generally defined as the process by which a surface is eroded by bombardment with accelerated ions; here the term "etching" is preferred for light or differential erosion while "ion-milling" signifies a more substantial ($> 2\,\mu$m, say) removal of material. For example, an incident

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5 keV argon ion would collide with and displace typically two or three host atoms [7, 8] (known as the "sputter yield") with no specific observable damage to the lattice. Although the idea of its use has been around for nearly a century [9], it has attracted recent interest [10–12, 16] as a technique of surface or thin film preparation for electron microscopy studies especially with non-metals, alloys, minerals and ceramics. In addition to its ion-milling potentialities, the technique's main features are its preferential etch-rates (with composite material or defect-laden structures) and considerable specimen heating which remains a disadvantage with organic or temperature-sensitive material.

In our studies we have used the more unorthodox saddle-field (cold cathode) ion source [13] using argon gas as a convenient supply of inert ions. Broad ($\sim 100\,mm^2$) or fine ($\sim 10\,mm^2$) ion sources could be chosen to rock over or be maintained at any required angle to the specimen which itself could be rotated during bombardment. Typical operating conditions would be $10^{-4}$ Torr pressure, 2 mA beam current at 5 kV beam energy. Typical rates of removal with unhydrated cement would be $\sim 0.1\,\mu m\,h^{-1}$ (broad source) and $\sim 1\,\mu m\,h^{-1}$ (fine source). Using mainly the broad ion source, a detailed investigation has been made into the effects of bombardment angle, specimen rotation and direction of etch on cementitious and other surfaces.

## 4. Results and discussion

It is now recognized that in addition to differential etching with composite materials, ion-beam etching can introduce surface artifacts. Differential etching can be minimized by using low (grazing) angles of the ion-beam on to the sample surface by virtue of the "self-shadowing" effect which predominates. The question of surface artifacts is somewhat more problematical, the main features being the production of surface cones obtained with stationary samples [14], and surface hummocks [10] with rotated samples. It was first noted by Fetz [15] that the sputtering rate was particularly angle-dependent reaching a maximum when the beam is at angle $\theta_{max}$ to the surface, this being about $\sim 30^\circ$ in the case of cementitious material. Barber *et al.* [16] have used Frank's kinematic theory of orientation-dependent dissolution of crystals in conjunction with the observed sputtering angle curve (of Fetz) to account for the growth of cones and hummocks. The theory predicts that when hummocks form during etching (due to some subsurface defect, say) they will particularly persist, growing laterally, when the sputtering angle is close to $\theta_{max}$. At these angles then, the surface hummocks may represent a planar map of subsurface defects including those "collected" from layers previously removed by the ion-etching. At larger (more normal) angles the angular sputtering dependence has the effect of magnifying, laterally and depthwise, minor depressions into significant troughs or holes.

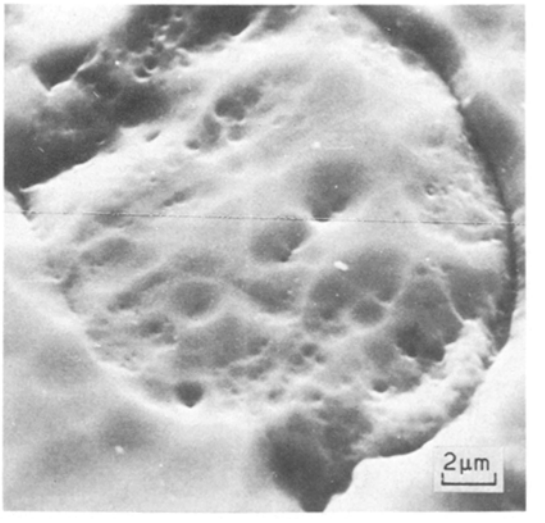



*Figure 1* SEM micrograph of an unhydrated cement section which has been subjected to ion-etching at normal incidence. Extensive undesirable etch pits and depressions are produced.

We have experimented using initially smooth, flat surfaces of mainly cement and rock (the sample preparation techniques are described elsewhere [17]) with and without specimen rotation and under argon ion bombardment using low-glancing (5° to 25°), medium (30° to 65°) and high-normal (70° to 90°) angles of incidence, the medium range including $\theta_{max}$. We can say that the overall trend of results is in good agreement with the general theory and predictions of Barber *et al.* [16], and we note some striking features as illustrated in the SEM micrographs: under high-normal ion-etch incidence, especially with the fine intense ion source, extensive etch pits (Figs. 1, 2a and b) are developed after a 0.5 to 1 μm etch (5 to 10 h) sometimes with large depressions containing needle-like features or relief on near-vertical side walls. At shallower etching angles

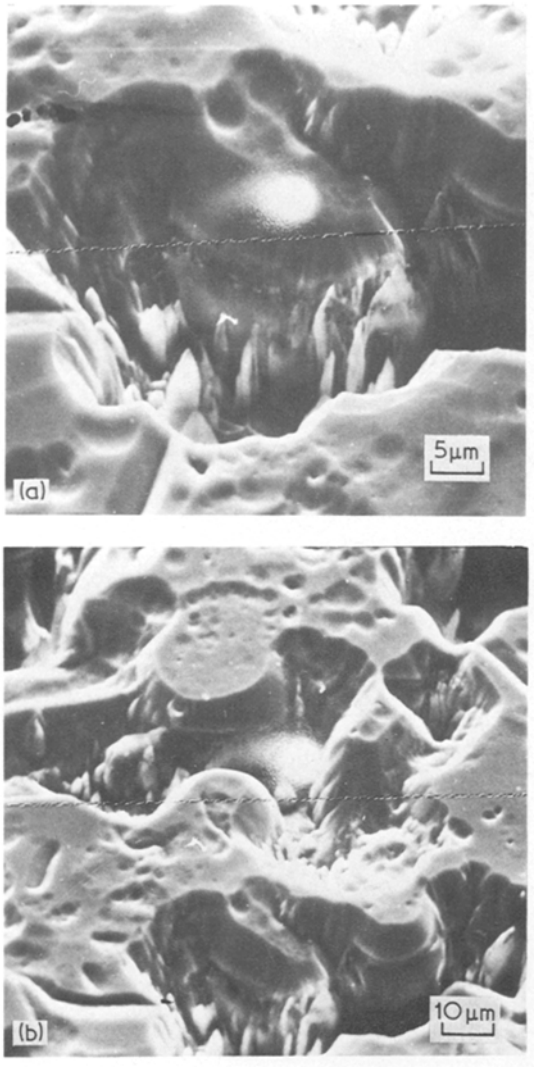



*Figure 2* SEM micrographs of an unhydrated cement section which has been subjected to ion-etching at normal incidence. Large depressions containing needle-like features on near-vertical side walls are evident.

with rotated samples, one obtains initially a well-defined etching of grain boundary or Griffith cracks if they are present (Figs. 3 and 4) and differential etching between the $C_2S/C_3S^*$ and interstitial phases (Fig. 5), the $C_2S/C_3S$ phases being etched at the faster rate (e.g., roughly one order of magnitude). Further etching reveals the familiar hummocky features which, as expected, grow in number and size with the duration of etching (Fig. 6). The hummocks are far more prominent in the interstitial material, being a generally less perfectly crystallized solid solution and even containing the occasional glassy phase. Further etching can yield significant depth profiles revealing isolated CaO or MgO inclusions and occasional dendritic belites, but attended by an undesirable increase in disfiguring hummocks. The total etching progression can be summarized in the following four stages:

(1) 0.2 to 0.3 μm etch (2 to 3 h). Grain bound-

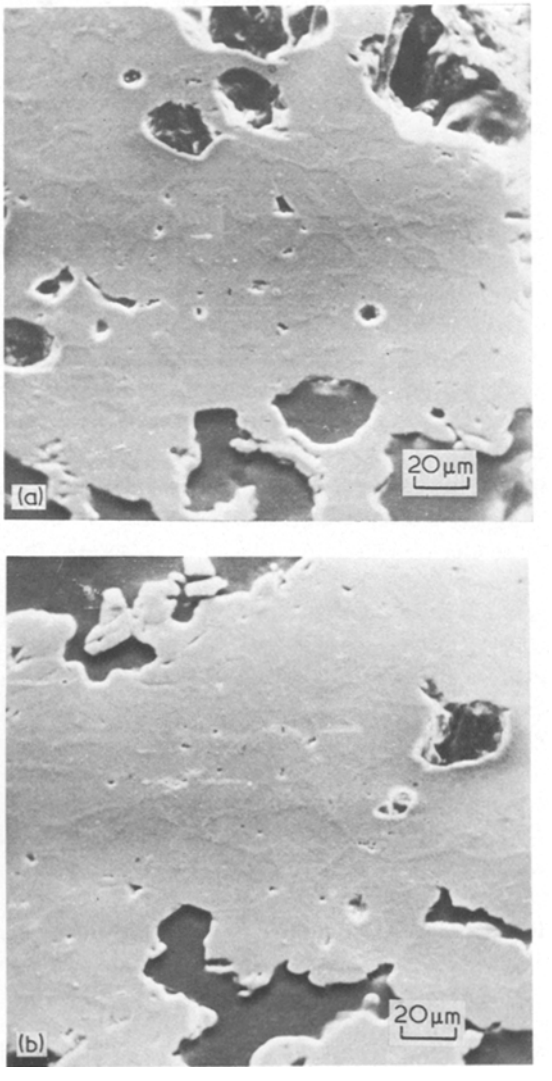
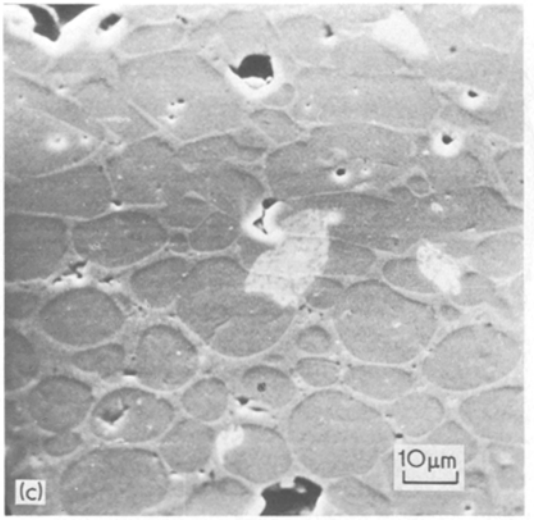



*Figure 3* SEM micrographs of an unhydrated cement section which has been subjected to light ion-etching at shallow incidence with rotation of the sample. Grain boundaries are clearly visible and phase delineation is easily achieved with minimum degradation of surface planarity of the cement grains. These conditions are ideal for SEM microanalysis work.

*Cement chemists' notation: C = CaO; S = $SiO_2$; A = $Al_2O_3$; F = $Fe_2O_3$.



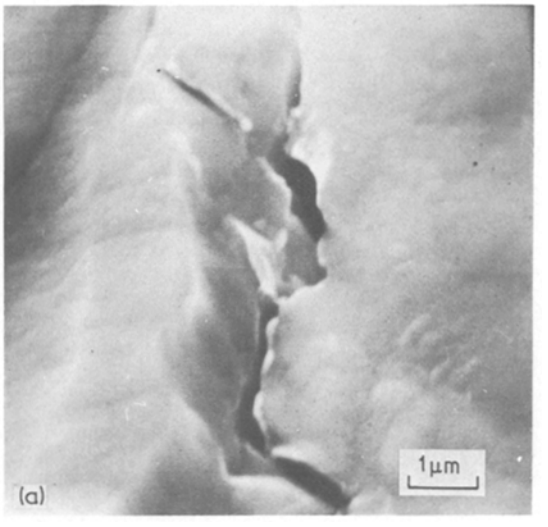




*Figure 3* continued.

ary etching – all surfaces, especially $C_2S/C_3S$ remaining essentially smooth and flat (Fig. 3).

(2) 0.5 to 1 μm etch (5 to 10 h). Differential etching – $C_2S/C_3S$ phases being removed faster than the interstitial phases which start to show hummocking (Fig. 5).

(3) 1 to 2 μm etch (10 to 20 h). Production of hummocks – the interstitial phase is thrown into higher hummock-laden relief; some hummocks also appear in the $C_2S/C_3S$ grains (Fig. 6).

(4) >2 μm etch (> 20 h). Depth profiling – etch is sufficient to reveal new zones of phase distribution but largely masked by the profusion of hummocks.

From the point of view of phase delineation coupled with accurate microanalysis, it is clear that the ideal conditions, as previously defined, are realized at only the first stage, i.e., with a "gentle" 0.2 μm etch at glancing (5° to 25°) incidence and rotation of the sample surface. Under these conditions, $C_2S/C_3S$/interstitial phase delineation is well defined without unwanted surface products or untoward (non-flat) surface relief as required for cement microanalysis studies. Occasionally differentiation between the $C_3A$ and $C_4A_pF_{1-p}$ ($0 \leqslant p \leqslant 0.7$) components of the interstitial phases is possible, though this is not generally so. Other features such as stress-induced cracks (as with deformed rock) may also be high-lighted.

Regarding ion-milling as a means of specimen thinning for electron transparency, the fine intense ion beam source has a positive but limited role.

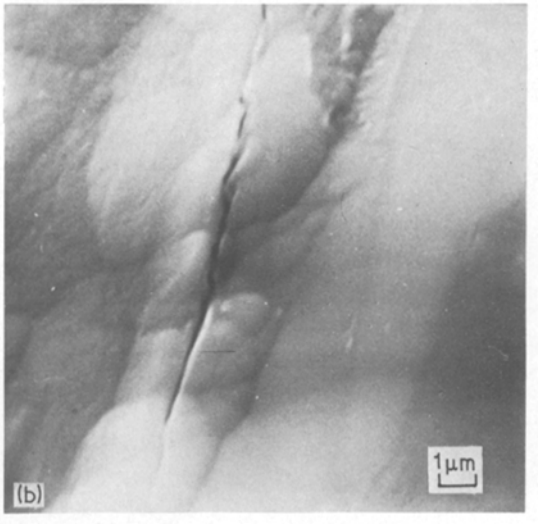



*Figure 4* SEM micrographs of a micro-granodiorite rock section which has been subjected to light ion-etching at shallow incidence with rotation of the sample. Micro-cracks of width < 0.5 μm are clearly visible.

Gross thinning is not practicable on account of the defect features described above and the differential rate of ion-milling. However, if cement clinker specimens can be accurately thinned mechanically to, say, 30 μm first, then ion-milling can be utilized as the final stage (< 1 μm) of preparation, though great care must be exercised to avoid catastrophic puncturing of the specimen by the ion beam. With such care one can prepare thin cement specimens suitable for conventional and high voltage electron microscopy.

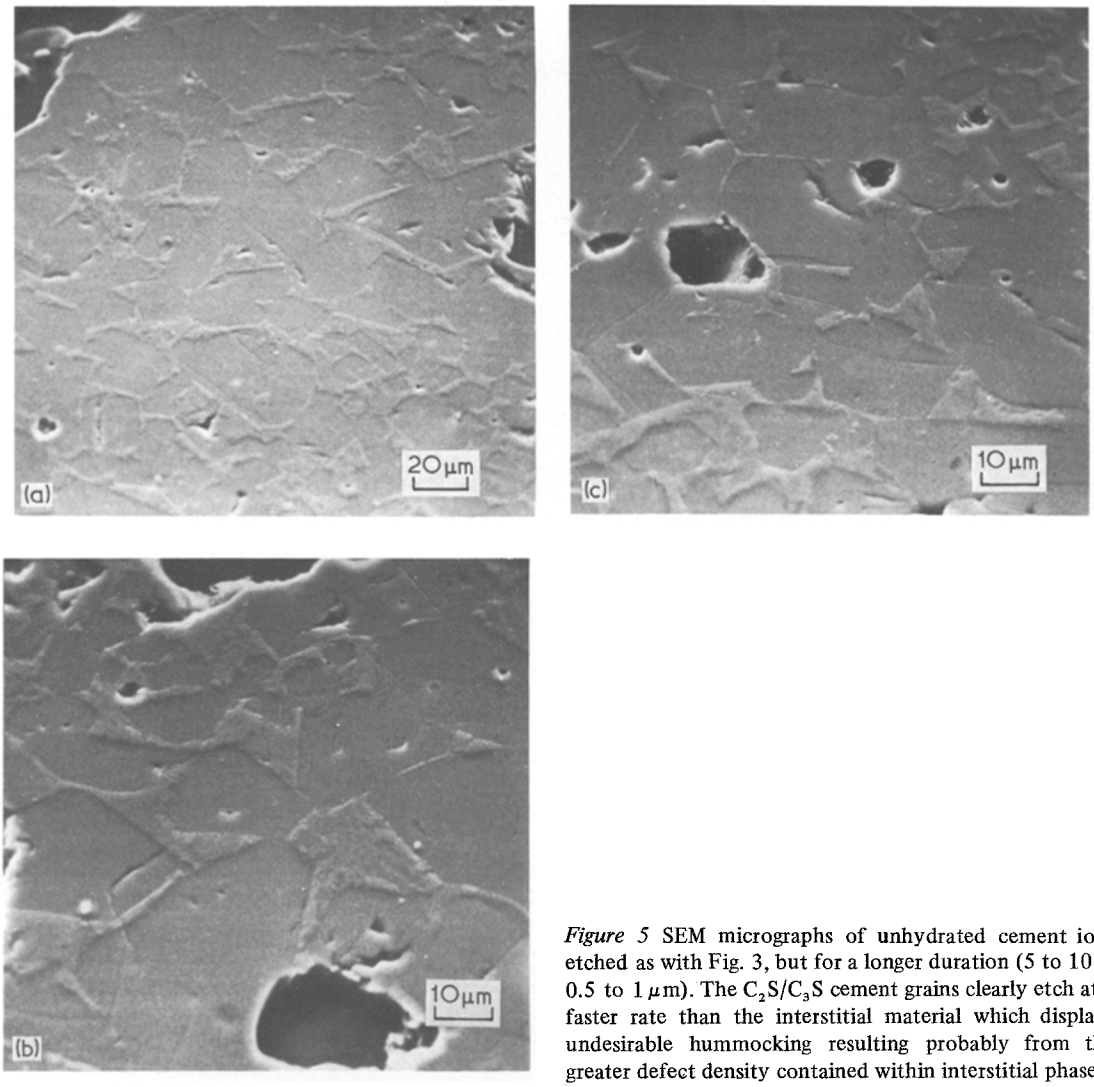



*Figure 5* SEM micrographs of unhydrated cement ion-etched as with Fig. 3, but for a longer duration (5 to 10 h, 0.5 to 1 $\mu$m). The $C_2S/C_3S$ cement grains clearly etch at a faster rate than the interstitial material which displays undesirable hummocking resulting probably from the greater defect density contained within interstitial phases.

## 5. Conclusions

Scanning electron microscope studies using ion-etching (broad source) and ion-milling (fine source) techniques on certain cementitious materials are in general agreement with the current theories of Barber *et al.* [16]: the differential etching of grain boundaries and between silicate and interstitial phases is pronounced, and the formation of hummocks reflects the density and accumulation of defects within the various phases. Under optimum conditions light etching of flat smooth sections will lead to clear unambiguous phase delineation while retaining the smooth, flat grains ideally suited for microanalysis. Similarly, micro-crack and fracture features can be faithfully revealed in stressed rock specimens. Lastly, ion-milling can also be successfully used as the final stage of preparation for cementitious specimens in transmission electron microscope studies.

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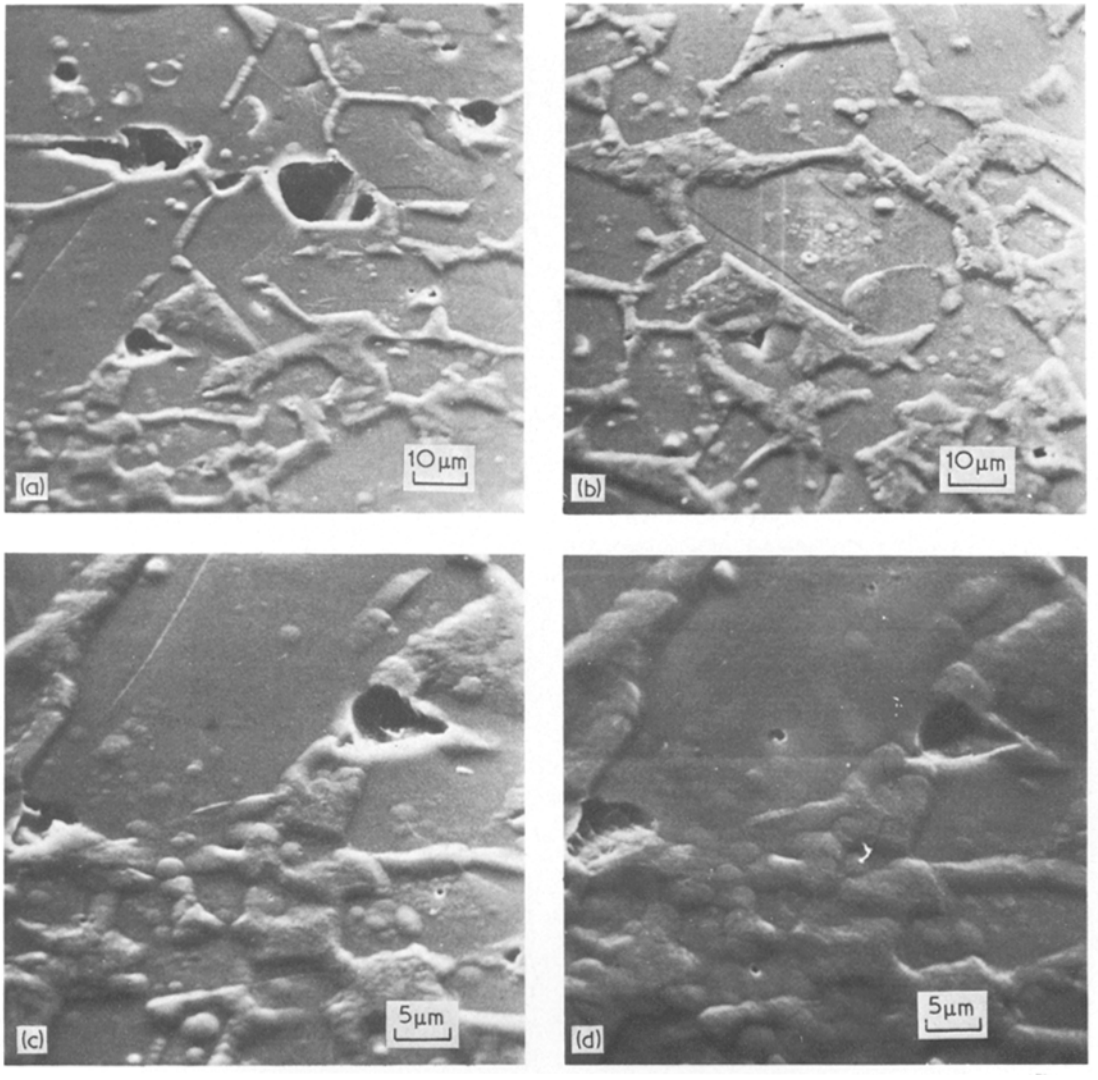


*Figure 6* SEM micrographs of unhydrated cement ion-etched as with Fig. 3, but for a much longer duration (10 to 20 h, 1 to 2 $\mu$m). The interstitial phase is thrown into high hummock-laden relief above the $C_2S/C_3S$ grains which also begin to show hummocking. (d) Shows a later stage of etching (20 h) of the same area displayed in (c) (15 h). These types of surface relief are most unsuitable for accurate microanalysis work on either $C_2S/C_3S$ or interstitial cement phases.

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