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Resolution of fine fibrous C-S-H in backscatter SEM examination

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Abstract

Secondary electron mode SEM images of hardened cement paste (obtained on fracture surfaces) have been published since the early 1970s. Most such images emphasized fine fibrous or dendritic C-S-H structures, which are commonly found in porous areas preferentially exposed by fracturing. Such fibrous structures are not generally seen in backscatter-mode SEM images obtained on polished surfaces. Examination with a high-resolution field-emission SEM (FE-SEM) instrument in the backscatter mode resolves these fibrous C-S-H structures, and suggests that failure to image them in conventional backscatter SEM is primarily due to inadequate resolution.

Keywords: Microstructure; Cement paste; Scanning electron microscopy; Hydration products

1. Introduction

The microstructure of hardened cement paste (hcp) has been studied by scanning electron microscope (SEM) methods for many years. Early SEM examinations were carried out using secondary electron SEM imaging on fracture surfaces of cement paste specimens. Secondary electron imaging modes were capable of high magnification, even in early instruments. It was found that dense areas of hcp yielded little information and were little studied. Porous areas were extensively imaged and were seen to include calcium silicate hydrate (C-S-H) structures composed primarily of fine fibrous particles.

Diamond [1] classified such particles as 'Type I C-S-H' and described them as being "typically anywhere from 0.5 μm to about 2 μm in length, and usually less than 0.2 μm across. Their outlines are usually not quite parallel, but narrow slightly toward their outer ends; often they branch into two or more portions at the outer tip. Short fibers seem to branch more extensively".

An extensive compendium of secondary electron micrographs of cement paste, most of them featuring such particles, was compiled by Williamson [2] as early as 1970.

Another morphological feature found by secondary electron SEM examination consisted of hollow shells representing thin-walled deposits around ground cement grains. It was evident that during hydration, the substance of the cement grain was dissolved from within such shells and precipitated elsewhere. Such hollow shell hydration features were first documented by Hadley [3], who found that the hollow shells were generally covered by a layer of short fibrous C-S-H. Some of Hadley's images were recently republished in more available form [4].

Starting in the early 1980s, secondary electron SEM investigations began to be superseded for most purposes by backscatter-mode SEM, as pioneered by Scrivener and Pratt [5]. Specimens for backscatter examination were prepared by epoxy impregnation, followed by precision sawing and careful polishing of a plane surface for examination. In contrast to the fracture surfaces examined by secondary electron SEM, these planar surfaces represented a random cross-section of the material, and were free of any bias toward preferential examination of porous areas. However, as indicated previously, the resolution possible

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with conventional backscatter SEM instruments is much less than the resolution available in the secondary electron examination mode.

Despite this limitation, examinations by backscatter SEM have been extremely useful, especially in examining the microstructure of mortars and concretes. Microscopic features observed by backscatter-mode SEM were recently reviewed by Diamond [6] and by Scrivener [7].

While many features are readily visible by both secondary electron and backscatter mode SEM examinations, the fibrous or branched fibrous C-S-H structures prominently featured in published secondary electron SEM examinations have not normally been seen in published backscatter SEM images.

In the present communication we report comparisons of conventional backscatter images of hcp with images taken with a field emission backscatter SEM (FE-SEM) capable of greater resolution than most backscatter-mode SEM instruments. The fibrous features previously seen by secondary electron SEM on fracture surfaces are detectable on plane polished surfaces by backscatter SEM, but only when the instrumental resolution is sufficiently high.

2. Comparison of images of C-S-H obtained by the different SEM techniques

Fig. 1, taken from [2] is one of the first secondary electron SEM images published, and shows the characteristic fibrous structures found in open porous areas on fracture surfaces of young Portland cement pastes. Practically identical images were subsequently published by many authors, including Diamond [1] and Scrivener [7]. In Fig. 1 the smaller branched fibrous particles are C-S-H; the large straight-sided rods are ettringite.

Fig. 2 is another secondary electron SEM image, reproduced from Hadley et al. [4]. This image shows a large hollow shell grain and a number of smaller bodies. The outer surface of the hollow shell, and the surfaces of the smaller bodies are all entirely covered with very well resolved fine fibrous C-S-H structures similar to those seen in Fig. 1.

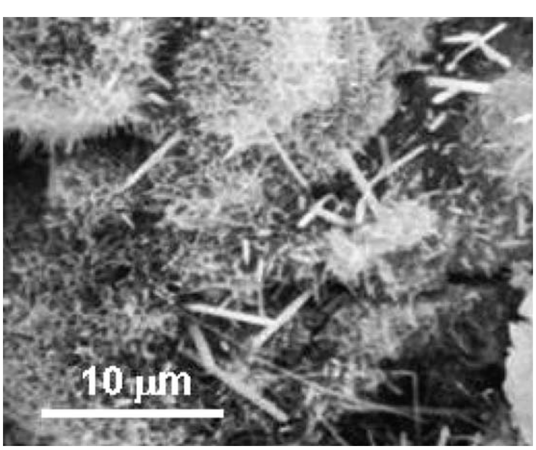

Fig. 1. Secondary electron SEM image of a porous area on a fracture surface of hcp. The shorter, branched fibrous particles are C-S-H; the larger rods are ettringite.

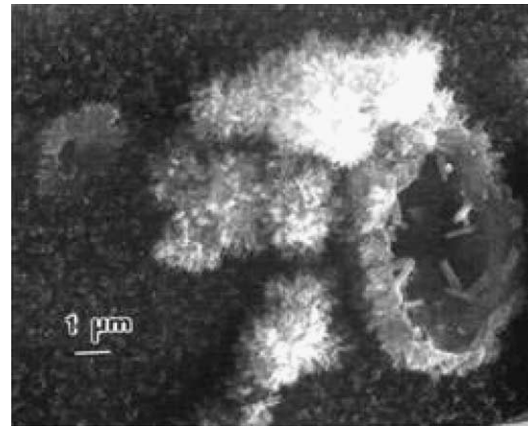

Fig. 2. Secondary electron SEM image of a hollow shell grain and associated C-S-H fiber structures.

In contrast to these images, Fig. 3 is a conventional backscatter SEM of a porous hcp area obtained on a polished surface. No indication is seen of the fibrous structures so prominent in Figs. 1 and 2. The apparent lack of detectable fine fibrous C-S-H structures is typical of nearly all published backscatter SEM examinations.

Much finer details of hcp structures have recently been imaged in backscatter SEM by Kjellsen and Justnes [8]. These authors used a field emission SEM (FE-SEM) that provides significantly higher resolution than most conventional backscatter instruments. Their specimen preparation employed epoxy impregnation and polishing in the usual manner, although a somewhat better than normal polish was required.

Fig. 4 shows an hcp as imaged by FE-SEM. The bright area marked "A" is a residual unhydrated portion of a cement grain; the area marked "B" is inner product C-S-H; and "D" is a small deposit of monosulfate. The outer product C-S-H, marked "C" clearly shows the presence of fine fibrous C-S-H structures, especially within the void in the lower right hand corner of the image. These structures are identical to those displayed in Figs. 1 and 2.

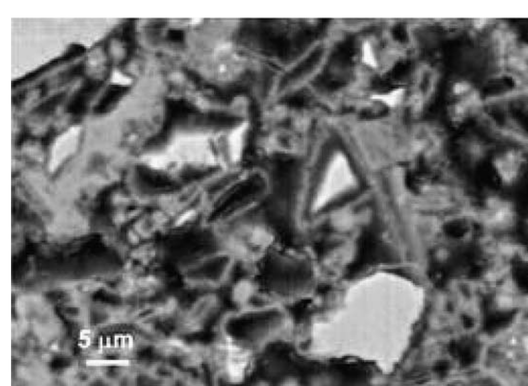

Fig. 3. Backscatter SEM image of porous area of hcp on a polished surface specimen. Note apparent absence of fibrous structures.

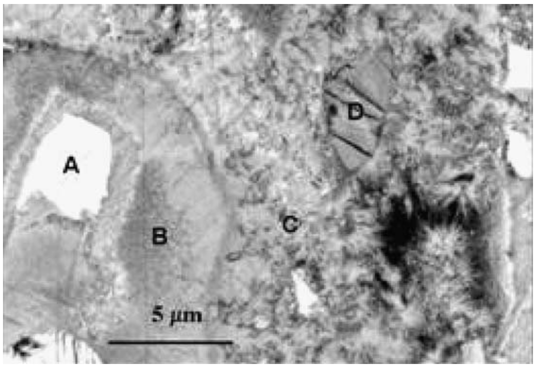

Fig. 4. FE-SEM backscatter image of an hcp specimen, showing the fibrous character of an area of outer product C-S-H (area "C"). Area "A" is a residual unhydrated cement core, area "B" is inner product C-S-H, and area "D" is monosulfate.

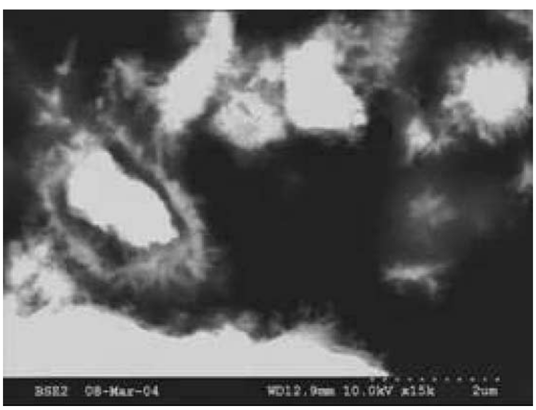

Fig. 5. FE-SEM backscatter image from a young hcp specimen, showing hollow shell grain and fibrous hcp structures similar to those seen in Fig. 2.

Fig. 5, taken from a very young (11 h old) hcp specimen imaged by FE-SEM, shows a hollow shell hydration grain and other hydrating grains covered with fine fibrous particles. The similarity to the structures seen in the secondary electron image of Fig. 2 is obvious.

3. Discussion

All of the SEM techniques image the same basic cement paste microstructure, but some of the details perceived are influenced by the nature of the specimen, and are limited by their different resolution capabilities. The fibrous character of much of the C-S-H in cement paste is easily imaged by secondary electron SEM, and less easily, by backscatter SEM of high enough resolution. Its failure to be detected by most conventional backscatter SEM instruments in part reflects the difficulty of recognizing such three-dimensional features when the image is restricted to a specific plane as by backscatter SEM, but mostly it is due to inadequate resolution. This must be kept in mind in interpreting the results of examination by conventional backscatter SEM.

Backscatter mode FE-SEM examination appears to provide an excellent means of imaging hcp (and concrete), since it combines high resolution of details with the ability to image representative surfaces free of the bias inherent in examining fracture surfaces. However, the high resolution requires extremely meticulous specimen polishing, and furthermore requires that low excitation voltage be used—usually 10 kV or less. Unfortunately, both requirements lead to serious limitations. The low excitation voltage renders energy-dispersive X-ray (EDS) analysis dubious for many elements; EDS is an essential adjunct for many SEM investigations, especially of concrete. Furthermore, the meticulous specimen polishing needed may be extremely difficult to achieve with mortar or concrete specimens which combine hard aggregate with much softer hcp. Thus conventional backscatter SEM retains its attractiveness for many investigations where the high resolution provided by FE-SEM backscatter examination is not required.

4. Conclusions

Examination of hcp in carefully polished backscatter SEM specimens using high resolution FE-SEM indicates that the "Type I C-S-H" fibrous structures originally seen to dominate porous areas of hcp by secondary electron SEM imaging can also be detected by backscatter SEM. Failure to do so in most backscatter SEM examinations appears to be due primarily to inadequate resolution.

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