Pergamon

Cement and Concrete Research 33 (2003) 611–616

CEMENT AND CONCRETE RESEARCH

Preparation of flat-polished specimens for SEM-backscattered electron imaging and X-ray microanalysis—importance of epoxy impregnation

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Received 14 June 2002; accepted 22 October 2002

Abstract

Representative and quantitative microstructural information of cement-based materials can be obtained in the backscattered electron and X-ray modes of the scanning electron microscope (SEM). One prerequisite, of several, is to use flat specimens. Microstructures that are minimally affected by the grinding and polishing necessary to produce the flat surface can be obtained. It is essential to fill the pores of the specimen with epoxy resin prior to grinding and polishing. After hardening, the epoxy stabilizes the microstructure and enables it to withstand the stresses of grinding and polishing without alteration. In the present paper, we describe a preparation technique that we consider to have produced excellent polished specimens. The importance of epoxy impregnation is demonstrated.

Keywords: Backscattered electron imaging; EDX; Microstructure; SEM; Specimen preparation

1. Introduction

While early scanning electron microscope (SEM) studies were performed primarily in the secondary electron mode, SEM studies today often use the backscattered electron or X-ray modes. Secondary electron images show essentially the morphological nature of the surface of a specimen. Often a fractured surface would be examined. The minimum requirement for specimen preparation and the apparent ease of interpreting topographical images make secondary electron imaging attractive. However, secondary electron images of fractured or sawn surfaces should be used with great caution. Since a crack propagates through the weakest portion of the material, a fractured surface is not representative of the material [1]. To take advantage of the analytical capabilities of the SEM (i.e., backscattered electron imaging/image analysis and X-ray microanalysis), a flat specimen is required [2]. The roughness of a fractured or sawn surface affects backscattered electron images and X-ray analyses adversely [1,3]. Unfortunately, the preparation of flat-polished specimens is relatively tedious, and requires special equipment and skills. However, once an artifact-free specimen has been produced, various phases of the cementitious material can be identified and quantified in the backscattered electron and X-ray modes. In addition, a flat-polished surface represents a random cross section of the specimen and, provided that coring and sectioning have been properly done, it can be representative of the material.

Proper preparation of flat-polished specimens for SEM is important. Severe artifacts can result from improper preparation [3,4]. The artifacts may appear as specific features in the backscattered electron mode, e.g., cracks introduced in cutting or drying. They may cause loss of microstructural detail and prevent good resolution. Damage to the specimen may take the form of plucking out of unhydrated cement grains or fracturing of the aggregates. Artifacts may cause the microscopist to misinterpret the microstructural features or composition of the specimens. Detwiler et al. [1] presented a general guide to the preparation of cementitious specimens for microscopic examination. Preparation protocols have also been presented (e.g. Refs. [3,5,6]). Examples of artifacts caused by improper preparation, and how these can be avoided or minimized, were discussed by Stutzman and Clifton [3] and Crumbie [4].

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PII: S0008-8846(02)01029-3

Epoxy filling of the pores is essential [3,7]. The hardened epoxy strengthens the microstructure, improving its ability to withstand mechanical preparation without fracturing, plucking out cement grains, or filling voids with debris. In addition, the required surface flatness can hardly be obtained unless the pores are filled with resin. Epoxy saturation can impart substantially improved contrast between the pores and solid phases. Preparation of high-performance cementitious systems can be particularly problematic due to their low permeability, which allows for only a very low impregnation depth of the epoxy. It is essential not to grind and polish beneath the intrusion depth of the epoxy. The present paper presents a preparation procedure that has provided flat-polished specimens of ordinary-performance and high-performance cement pastes and concretes [8–12] with a minimum of artifacts. The importance of epoxy impregnation is discussed in particular, and epoxy intrusion depths are reported. It is demonstrated that hollow shells pores (i.e., Hadley grains) are real features of the microstructure and not results of particle plucking.

2. Specimen preparation

2.1. Materials

Paste specimens were produced. The binders comprised a low-alkali sulfate-resistant cement with 0% or 10% silica fume by mass. The water/binder (w/b) ratios were 0.25 and 0.40. A superplasticizer was used to obtain appropriate workability. Further details of the material characteristics are given in Ref. [10]. The mixing procedure is described in Ref. [13]. The pastes were cast in PVC tubes 27 mm in diameter. The openings were closed with rubber stoppers. The molds were rotated slowly for 1 day under water to prevent segregation. The specimens were cured under sealed conditions (i.e., in their molds) for 3 months. Mixing and curing took place at 20 °C.

At 3 months, the pastes were cut into cubes a few millimeters in size. A precision diamond splitting wheel was used for the sectioning. Ethanol was used as lubricant. The specimens were submerged in liquid nitrogen and later freeze-dried. With respect to impregnation and curing/polymerization of the epoxy, it is important that the specimens be dry.

2.2. Preparation procedure

2.2.1. General

The mechanical preparation of flat-polished specimens involves essentially a series of grinding and polishing steps performed with progressively finer abrasives. A gradually smoother surface is obtained as each grinding and polishing stage successively removes the deformation produced by the previous stages of preparation. Ultimately, the specimen surface should be flat. However, since the constituents of cement-based materials are abraded at different rates due to their different hardness, some topographic difference is inevitable. However, keeping polishing times short minimizes relief, with its detrimental effects on backscattered electron imaging and X-ray microanalysis. It is essential to preserve the pore structure and to stabilize the microstructure with epoxy resin before grinding and polishing [3,7]. As we will show later, microstructures that were not supported by epoxy resin exhibited extensive particle plucking, pitting, and microcracking.

2.2.2. Initial stages

After drying, the face of the sample to be polished is subjected to an initial dry grinding on a fine emery paper. This is done to ensure a plane surface. The next step involves casting of the sample in epoxy resin. A bakelite ring form (diameter 25 mm) is attached to the inside of a plastic mounting cup while the sample is placed on a plane Teflon disc on the bottom of the cup with its plane surface down. Epoxy is then poured into the mold. We use a low-viscosity epoxy resin (EPO-TEK 301) for mounting as well as for later impregnation. The epoxy is cured at 40 °C for at least 24 h. To remove the epoxy that may have intruded underneath the plane surface of the sample during casting and to retain a plane surface, the specimens are ground dry on a diamond wheel (90 μm grit). The specimen is then ground on diamond discs of 30 μm and then 15 μm grit. Ethanol is used as the lubricant and the specimens are cleaned ultrasonically in ethanol to remove any material deposited on the surface. The specimens are dried at around 40 °C to evaporate the ethanol. At this stage, the thickness of the specimens is measured by a high-precision caliper to the nearest 10 μm.

2.2.3. Epoxy impregnation

The specimens are then vacuum-impregnated with the epoxy resin. To remove entrapped air from the epoxy, it is placed in a vacuum chamber that is evacuated by a water jet pump prior to impregnation. The specimen obtained, as described in Initial Stages, is placed with its face up in a vacuum chamber that is pumped down to 30 mbar. The epoxy is fed from its cup outside the vacuum chamber to the top of the specimen via a plastic tube. The quantity to be dispensed is regulated by a valve. The face of the specimen is covered with epoxy. After about 10 min, air is let gradually into the vacuum chamber to push the epoxy further into the pore system of the specimens. The epoxy is cured at atmospheric pressure at 40 °C for at least 24 h.

2.2.4. Final stages

The impregnation is followed by very careful grinding, lapping, and polishing. To remove surplus epoxy and to

retain the plane surface of the specimen, the first grinding stage is dry grinding on the 90-μm diamond wheel. The specimen is ground to a thickness about 30 μm larger than the initial thickness (cf. Section 2.2.2), as measured by the caliper. The final grinding stages involve grinding on diamond discs of 30 μm and then 15 μm. Ethanol is used as lubricant. Lapping is performed with ethanol/diamond grit suspension (8 μm) on a glass wheel. Extreme care must be taken not to remove too much material during grinding and lapping.

The first two polishing stages are performed on very hard wheel coverings (MD-Plan; Struers) with two grades of ethanol/diamond polishing grit suspensions (6 μm and then 3 μm). The two final polishing stages are performed on hard wheel coverings (MD-Dur; Struers) with two grades of ethanol/diamond grit polishing suspensions (1 and 0.25 μm). Polishing is performed with moderate force and at a low rotation speed. Each polishing stage is generally carried out for no longer than 2–4 min. After each stage, the specimens are cleaned ultrasonically in ethanol to remove the grit. To avoid dissolution of water-soluble phases, one should always use nonaqueous lubricants for cutting, grinding, lapping, and polishing.

To assess the effect of the various preparation stages, we have found it useful to examine the specimens in an optical microscope in the reflected-light mode. As light will be reflected from plane surfaces, a bright homogeneous field of view indicates a plane surface. Cavities and scratches in the surface will absorb light and appear as darker stains or scratches. Fig. 1 shows an image of a polished cement paste with a high degree of flatness. Fig. 2 shows a specimen that has been ground below the intrusion depth of the epoxy. There are numerous cavities unsaturated with resin. These deviations from flatness appear darker gray.

The polished specimens need to be sputter-coated with a thin film of conductive material (such as carbon) to prevent the build up of electric charge when the specimen is scanned by the electron beam. The specimens are preserved in desiccators with silica gel prior to and after examinations to prevent hydration or carbonation.

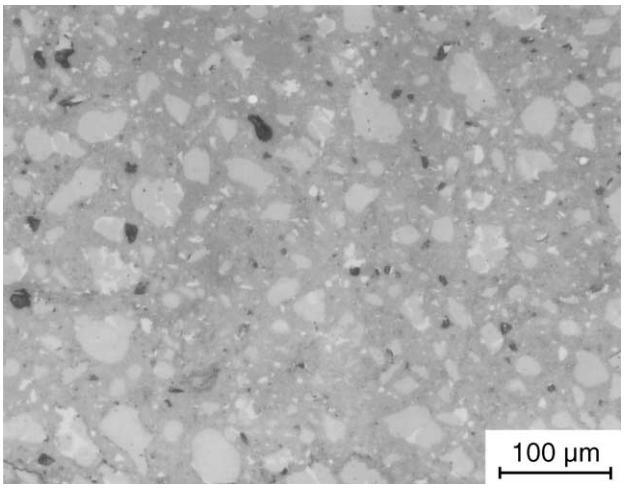

Fig. 1. Optical microscope image of polished cement paste. Good preparation.

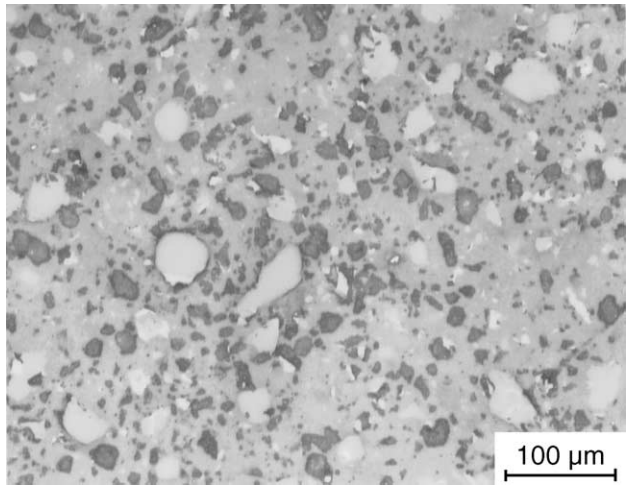

Fig. 2. Optical microscope image of polished cement paste. Poor preparation.

2.2.5. Specimens for evaluation of the epoxy intrusion depth

A major objective of the present paper has been to evaluate how deep the epoxy intrudes into the sample. The casting normally performed before impregnation (cf. Section 2.2.2) was omitted. Paste samples were placed inside the bakelite ring form. After evacuation of the vacuum chamber, the bakelite ring form assemblage was filled with epoxy resin and all faces of the sample were impregnated as described in Section 2.2.3. The surface that was to be polished was overground to ensure removal of the resin-filled upper surface. This left a polished surface with an outer rim impregnated with epoxy and the interior unsaturated. Grinding, lapping, and polishing were otherwise performed as described in Section 2.2.4. The epoxy-saturated outer portion was generally clearly distinguishable

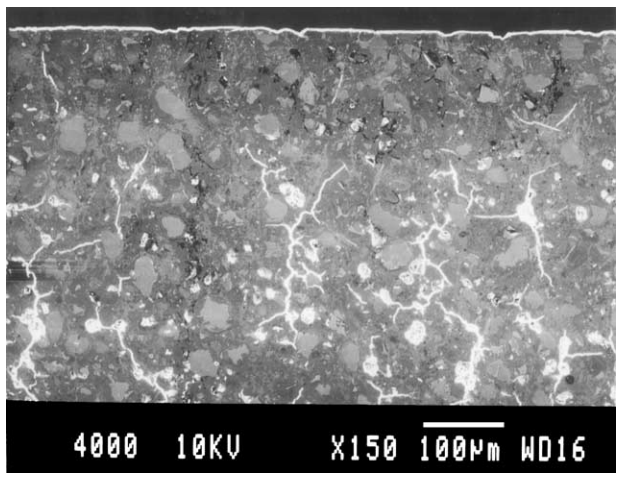

Fig. 3. SEM—secondary electron image of the 0.40 w/b ratio paste without silica fume.

Table 1
Observed epoxy intrusion depths of the paste specimens

Mix w/b ratio	Silica fume (%)	Intrusion depth (μm)
0.40	0	120
0.40	10	100
0.25	0	70
0.25	10	40

from the unsaturated interior, making direct observations of epoxy intrusion depths possible.

3. Results and discussion

3.1. Epoxy intrusion depth

Fig. 3 depicts a secondary electron image of the 0.40 w/b ratio paste without silica fume.

The edge is seen towards the top of the image. The outer (approximately) 120 μm of the specimen is saturated with epoxy resin, as can be seen by the darker color. The brighter interior is unsaturated with epoxy resin. Pores, cavities, and microcracks not filled with epoxy resin light up in the secondary electron mode, since electrons tend to accumulate on the edge of cracks and cavities and at high spots. On the other hand, electrons will be conducted away on a flat, coated surface. Thus, charging does not occur at the edges of pores or cracks filled with resin. The saturation of pores and cracks with resin can be seen in the secondary electron mode (Fig. 3).

While the intrusion depth of the 0.40 w/b ratio paste without silica fume appeared to be about 120 μm overall, in areas of penetrating microcracks or increased porosity, the intrusion depth was up to a few hundred microns. Table 1 shows the observed epoxy intrusion depth of the various paste specimens. The results are based on studying a number of secondary electron images similar to that of

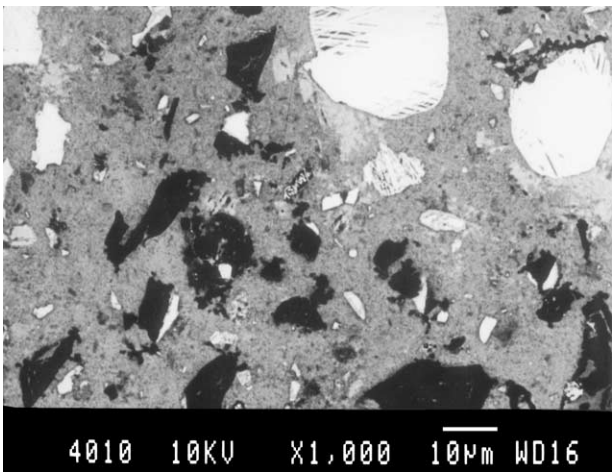

Fig. 4. SEM—backscattered electron image (compositional) of the 0.40 w/b ratio paste with silica fume. From outer part of paste section, saturated with epoxy resin.

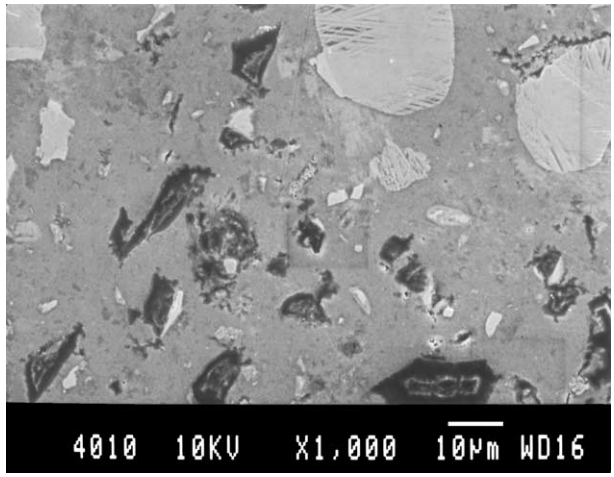

Fig. 5. SEM—secondary electron image of the field from Fig. 4. From outer part of paste section, saturated with epoxy resin.

Fig. 3. The numbers represent the approximate depth to which practically all areas of the surface appear saturated with resin. The observed intrusion depths are very small, and decrease with decreasing w/b ratio and the presence of silica fume. It is clear that extreme care must be taken during grinding and polishing not to remove the epoxy-saturated surface.

3.2. The importance of epoxy impregnation

Both clear and obscure boundaries between phases may exist in cement-based materials. Loss of definition due to plastic deformations ('smearing') from mechanical preparation may occur with metals, but is less likely to occur in brittle materials such as cement and concrete [3]. Microcracking, fracturing, and pitting are the most common artifacts according to our experience. Contrast between features is reduced by poor mechanical preparation. Intermixed phases cannot be separated, and feature clarity

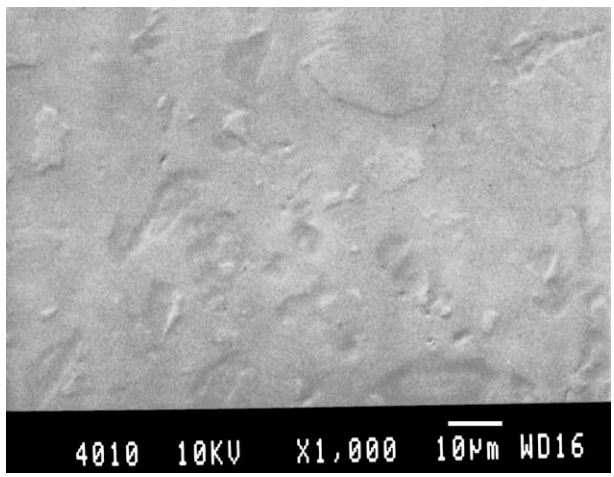

Fig. 6. SEM—topographic backscattered electron image of the field from Figs. 4 and 5. From outer part of paste section, saturated with epoxy resin.

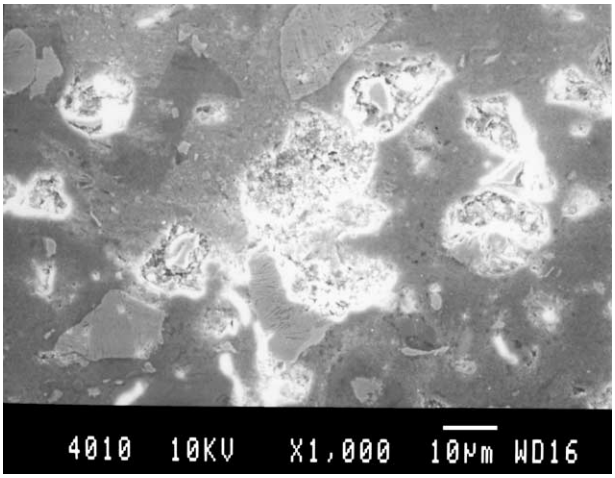

Fig. 7. SEM—secondary electron image of the 0.40 w/b ratio paste with silica fume. Interior part of paste section, unsaturated with epoxy resin.

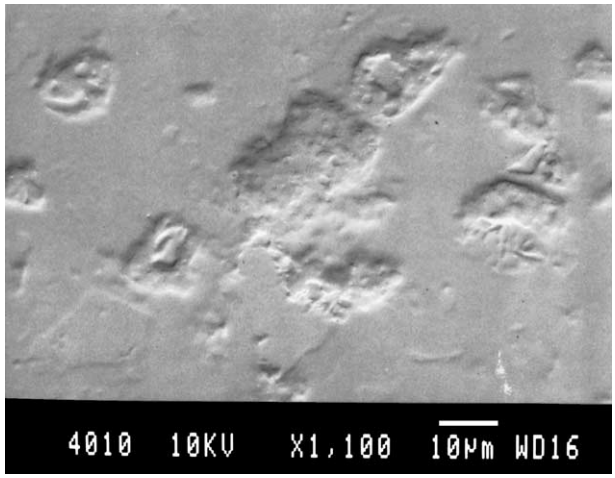

Fig. 8. SEM—topographical backscattered electron image of the field from Fig. 7. Interior part of paste section, unsaturated with epoxy resin.

cannot be improved. Thus, when phases can be clearly separated in the backscattered electron mode and the specimens are flat, this is a strong indication that the microstructure has not been altered due to the preparation. Weakly defined phases may represent the original microstructure in specimens that are flat and free of fracturing and pitting.

Fig. 4 is a backscattered electron image of the 0.40 w/b ratio paste with 10% silica fume showing clear microstructural definition. There are clearly defined boundaries between unreacted cement grains (bright particles) and reaction products (gray phase), as well as between the large pores (black) and reaction products. Fig. 5 shows a secondary electron image of the field from Fig. 4. The field is close to the edge of the specimen and represents an area saturated with epoxy resin. There is little topographic variation in the secondary electron image (Fig. 5) and in the topographic backscattered electron image[1] (Fig. 6). The topographic backscattered electron image shows the topographic appearance of the specimen surface. Some topographical relief is observed between phases (Fig. 6). As discussed previously, topographic relief cannot be completely avoided because the phases have different hardness. The secondary electron image (Fig. 5) reveals that the electrons do not accumulate in the pores, indicating that they are filled with epoxy resin. As discussed previously, electrons tend to accumulate in empty pores. If the pores are filled with resin, the epoxy resin bridges the pore and prevents charging. The appearance of distinct microstructural features, as in the backscattered electron image of Fig. 4, and the presence of a flat surface with epoxy-impregnated pores (Figs. 5 and 6) show that the microstructure was practically unaltered by the preparation.

As impregnation was performed before grinding and polishing, it becomes evident that the larger resin-saturated pores, up to about 10 μm across, are not artifacts of the mechanical preparation steps but real features of the microstructure. Thus, they cannot be a result of particle plucking. The impregnation has filled these large original pores with resin and has preserved them to withstand the subsequent grinding and polishing. These large resin-filled pores observed in Fig. 4 are essentially of the Hadley grain type or hollow shell type, which are discussed elsewhere [9,10].

Fig. 7 shows a secondary electron image, depicting an area from the interior part of the same specimen below the depth of epoxy saturation. As pores are no longer filled with epoxy resin, the bottom of the cavities is clearly revealed in

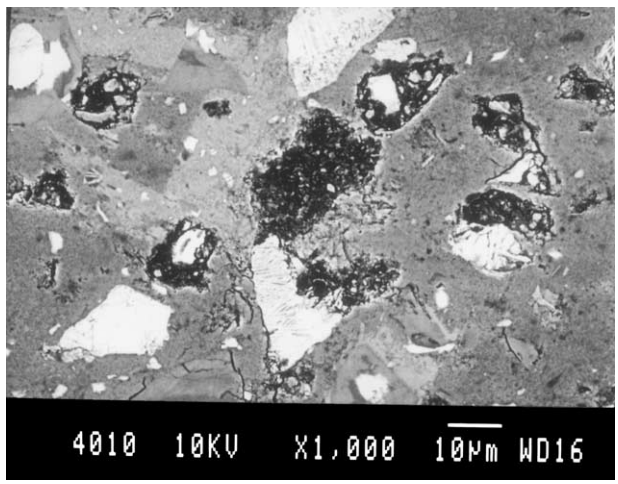

Fig. 9. SEM—backscattered electron image (compositional) of the field from Figs. 7 and 8. Interior part of paste section, unsaturated with epoxy resin.

[1] The topographic backscattered electron mode is obtained by subtraction of the signals from the semiconductor element detector. The more common compositional mode showing the atomic number contrast is obtained by addition of the signals.

the secondary electron mode. The lack of flatness and a discontinuous conductive coating cause charging. Fig. 8 depicts a topographical backscattered electron image of the same field. The lack of epoxy in the cavities is seen as a much larger topographical distortion than the normal relief effects observed between phases of different hardness (i.e., Fig. 6).

Clear microstructural definition was observed in the area of the specimen that was saturated with epoxy (Figs. 4–6). Fig. 9 shows the backscattered electron image of the field depicted in Figs. 7 and 8, which was not saturated with epoxy. The lack of microstructural definition becomes apparent. The distinct pores that were observed in the epoxy-filled portion are no longer visible; instead, parts of the microstructure appear fractured and eroded. As this lack of microstructural contrast was not seen in the epoxy-saturated portion of the specimen, it becomes apparent that grinding has resulted in particle plucking and pitting. Unsupported portions of the microstructure have been abraded away during grinding and polishing. These artifacts also occurred in the epoxy-saturated portion of the specimen, to a much lesser extent. We recommend that SEM studies of flat-polished sections be preceded by an examination in the topographical imaging modes to aid in the detection of artifacts. Thus, misinterpretations of the microstructure can be avoided.

4. Conclusions

Backscattered electron imaging and X-ray analysis of cementitious materials in the SEM require epoxy-impregnated, flat-polished specimens. A protocol for the preparation of this type of specimens of ordinary-performance and high-performance cement-based materials is presented. The preparation implies essentially vacuum impregnation with epoxy resin, followed by mechanical grinding and polishing with progressively finer abrasives. The epoxy fills the pore space and, after hardening, supports the microstructure during the mechanical preparation. It is found that microstructures unsupported with resin exhibited extensive pitting, fracturing, and microcracking. These artifacts were practically eliminated when the microstructure was saturated with epoxy resin. It is convenient to use the topographical imaging modes in the SEM to examine the specimen for these types of preparation artifacts. Epoxy intrusion depths were found to be in the range of 40–120 μm, depending on the mix formulation of the paste specimens. Grinding must thus be performed with care so as not to grind beneath the intrusion depth of the resin. Since epoxy impregnation is performed ahead of grinding and polishing, it becomes evident that pores filled with epoxy resin are real features of the microstructure, and not a result of particles being plucked out during preparation.

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