Irradiation Damage of Nano-C$_2$S Particles Studied by In-Situ Transmission Electron Microscopy

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Abstract: Development of a reactive nanocement is a new approach to improve the physical and chemical properties of construction materials. However, due to the decreased size of cement particles, beam damage during transmission electron microscope (TEM) observation becomes more severe than in conventional cement. In this work, irradiation damage to nano-C$_2$S (dicalcium silicate) is observed and studied by in-situ evolution of diffraction patterns (DP), high resolution TEM (HRTEM), and electron energy-loss spectroscopy (EELS). The results show that the damage to nano-C$_2$S occurs through a decomposition reaction. Nano-C$_2$S is first amorphized, and then re-crystallized into CaO nano-crystals with average size of 7 nm surrounded by an amorphous matrix of Si and SiO$_2$. During this process, C$_2$S particles exhibit volume shrinkage. The damage energy causing the reaction was analyzed and electron-electron inelastic scattering produced radiolysis and heat, leading to the observed phenomena.

Key words: Nanocement, TEM, damage, inelastic scattering, decomposition.

1. Introduction

Cement is a mixture comprised of different components, i.e., C$_3$S, C$_2$S, C$_3$A, and C$_4$AF (where C = CaO, S = SiO$_2$, A = Al$_2$O$_3$, F = Fe$_2$O$_3$), among which dicalcium silicate (C$_2$S) is one of the major components. However, due to its slow hydrating nature, C$_2$S is usually used to provide long-term durability of concrete, and its early strength is mostly dependent on other minerals, such as C$_3$S and C$_3$A. A need to obtain a reactive form of C$_2$S mineral is based on this consideration. By improving its reactivity, C$_2$S may participate in early strength evolution and has the potential to improve medium term hydration as well. The development of nanocement [2, 7, 8] brings focus to this goal. An early age reactivity could be increased tenfold through exposing much more reacting surface area compared with conventional cements [8]. Based on this idea, nano-sized C$_2$S was therefore fabricated through a chemical combustion method. To understand the hydration properties of nano-C$_2$S, the precursor powder must first be well characterized. Transmission electron microscopy (TEM) is a commonly used tool for characterization of nanoparticles. However, with TEM we have to assess the extent of irradiation damage caused by the electron beam to electrically-insulating cement specimens [6, 9, 10]. In this work, beam damage of nano-C$_2$S particles was characterized during TEM observation and methods to reduce the damage are proposed.

2. Experimental

Nano-C$_2$S was synthesized from limestone and other naturally occurring materials by NanoDynamics (www.nanodynamics.com), using a chemical combustion reaction that is initiated at approximately 300ºC versus the 1500ºC used in the preparation of conventional cement. The microstructure and phases of the nano-C$_2$S were characterized by scanning electron microscopy (SEM, FEI Quanta 3D dual-beam system), X-ray diffraction (XRD, Bruker D8 instrument), and the MAUD Rietveld method [1]. To prepare TEM
samples, particles were ultrasonically dispersed into 100% alcohol to form a suspension. Then a cement sample was obtained by dipping a carbon-coated copper grid support into the suspension for one second. TEM characterization was performed using Tecnai 20 (FEI) operating at both 200 kV and 120 kV with a LaB₆ filament and Titan 80-300 (FEI) at 300 kV with a Field Emission Gun (FEG).

3. Results and discussion

The typical morphology of the nanocement in Fig. 1a consists of lightly agglomerated nanoscale particles with an average size of 100 nm, in contrast with the typical particles of ordinary Portland cement (OPC) shown in Fig. 1b. The XRD pattern shown in Fig. 1c indicates that the dominant phases of the nanomaterial as C₂S and CaCO₃ (Fig. 1c) with the analysis shown in Table 1.

Characterization by TEM is performed with uniformly dispersed cement particles. Beam damage induced phase transformation of small particles (less than 100 nm) occurred essentially instantaneously on exposure to the beam, much too fast for the reaction path to be determined. Thus larger ones (no less than 100 nm) were chosen to study the chemistry before radiation since the damage to them occurred more slowly. Elements Ca, Si, O were observed from the EELS (Electron Energy Loss Spectroscopy) spectra (Figs. 2a–2c), which indicates the composition of the particle in Fig. 2b is C₂S rather than CaCO₃. After electron irradiation, the resulting microstructure of the particle is shown in Figs. 2d–2g. Fig. 2e is a high-resolution image taken from the region indicated by the arrow in Fig. 2d, demonstrating that the damaged particle consists of nano-sized subgrains with an average size of around 7 nm. Fig. 2f is a fast Fourier transformation (FFT) of the region in (b), which matches the selected-area diffraction pattern (SADP) in (g). The diffraction pattern can be indexed to the cubic CaO phase, indicating that a decomposition reaction transformed the C₂S to CaO and a siliceous product under electron beam irradiation.

<table>
<thead>
<tr>
<th>Phases</th>
<th>Proportion in nanocement (Wt%)</th>
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<tbody>
<tr>
<td>C₂S</td>
<td>82.65</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>13.79</td>
</tr>
<tr>
<td>Others</td>
<td>3.56</td>
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</tbody>
</table>

Fig. 1  SEM image of a typical nanocement (NC) aggregate (a) comparing with a particle of ordinary Portland cement (OPC) in (b). XRD pattern in (c) showing the principal phase of nanocement. A-C₂S; B-CaCO₃.

Fig. 2  EELS spectra of the cement particle in (d) before radiation damaged: (a) Ca, (b) Si, and (c) O. The existence of Si demonstrated the composition of the particle in is C₂S other than CaCO₃. (d) - (g) are the characterization of damaged products of the particle in (d). (e): high resolution image of the arrow indicated region in (d); (f): fast Fourier transformation (FFT) of image (e); (g): selected-area diffraction pattern. The index of rings in (f) and (g) indicates the existence of CaO after radiation.
In-situ observation of the phase transformation process of nano-C$_2$S was illustrated by a series of diffraction patterns in Figs. 3a–3f. Initially, a bright diffraction pattern near the T00 zone axis were observed (Fig. 3a). The corresponding particle morphology is shown in Fig. 3g. With irradiation, the diffraction spots became weak due to the partial decomposition of C$_2$S [see spots in (b)], until most of the spots disappeared and an amorphous pattern was obtained after 29 min of irradiation (Fig. 3c). The particle corresponding to the pattern in Fig. 3c is shown in Fig. 3h. Amorphization is considered to be one of the signs of being radiation damaged. Similar phenomenon was observed in C-S-H phase in Ref. [6]. Volume shrinkage was also observed during the process [regions indicated by the black arrows in (g)]. After 36 min, new diffraction spots started to form (black arrows in Fig. 3d), suggesting the formation of new crystals. More spots appeared after 50 min of irradiation, indicating additional crystallization (Fig. 3e). Finally at 89 min, a well-shaped CaO polycrystalline ring pattern was obtained with the corresponding microstructure seen in Fig. 3i. The particle showed additional volume shrinkage, as shown in Fig. 3h (See regions marked with arrows in (h)).

Fig. 4 shows the decrystallization process of C$_2$S in high-resolution mode using the Titan TEM. In order to have the time resolution to observe the reaction, a thicker region from a relatively large particle was chosen. At 0 min, a perfect crystal lattice was observed in the region circled by a dashed line (Fig. 4a). The lattice spacing is measured to be 0.261 nm, characteristic of C$_2$S, not CaCO$_3$. At 14 min of irradiation, partial amorphization has occurred (Fig. 4b) with close to complete amorphization after 16 min (Fig. 4c). During this process, CaO phase was not observed, most probably because the CaO nano-crystals formed in a different focal plane. The focal distance in high-resolution imaging is quite short (of order several nanometers), and thus it is not always possible to imagine multiple regions of a three-dimensional particle concomitantly with this approach.

Decomposition of C$_2$S results in the formation of CaO in form of nanocrystals. Electron energy loss spectroscopy (EELS) was performed using the silicon L edges to investigate the form of the siliceous decomposition product. Each spectrum presented in...
Fig. 5 was recorded for 10 s. Initially, distinct Si-$L_{1,2,3}$ edges were observed, which suggests the existence of Si$^{4+}$. The broad peak observed at about 131 eV was likely due to an inner-well resonance [11]. Five minutes later, the intensities of the Si-$L_{1,2,3}$ edges started to decrease, and continue to decrease with irradiation time. After 12 minutes of irradiation, an identifiable shoulder near 100 eV appeared, indicating the formation of Si$^0$ [3]. The shoulder became more distinct with time. After 66 min of irradiation, both Si$^0$ and Si$^{4+}$ were observed although the Si-$L_{1,2,3}$ edges became more flat. Combining these results with the images of the microstructures in Figs. 2 and 3, we conclude that Si$^0$ and Si$^{4+}$ are associated with the formation of amorphous Si and SiO$_2$ nanoscale phases, a result that is consistent with the observations of the development of diffuse scatter in the diffraction patterns.

We investigate the effect of electron voltage in order to further elucidate the mechanism of beam damage. Electron irradiation can lead to sample damage through several mechanisms, such as sample heating, knock-on (displacement) damage and radiolysis (bond breaking) [4, 5]. The gradual amorphization observed in Fig. 3 is consistent with a transformation from a crystalline lattice to an amorphous state, and suggests that electron-electron inelastic scattering is leading to radiolysis during irradiation of C$_2$S, while with further irradiation, the atoms reconfigure to form CaO. In general, radiolysis can be minimized by using the highest available accelerating voltage to reduce the inelastic scattering cross section [4, 5]. We found that the reaction rate was slower with a voltage increase from 120 kV to 200 kV using the Tecnai 20, a result consistent with radiolysis being the primary damage mechanism. Other ways to reduce the damage are using a smaller condenser aperture or taking pictures at lower magnification since both reduce the dose reaching the sample. Another form of damage to C$_2$S particle is through direct heating by the beam [5] since C$_2$S is a ceramic with low thermal conductivity. Beam heating may also lead to the observed volume shrinkage and the mass loss of C$_2$S particle shown in Fig. 3. To reduce beam heating-induced damage, carbon coating both sides of the TEM sample surface should help.

4. Conclusion

Beam damage to nano-C$_2$S particles during TEM observation was systematically investigated. C$_2$S particles are first amorphized, and then re-crystallized into CaO nano-crystals with average size of 7 nm surrounded by an amorphous matrix of Si and SiO$_2$. The reaction pathway suggested that the primary damage was radiolysis induced by electron-electron inelastic scattering. Beam-induced heating was determined to be a secondary cause of damage, leading to volume shrinkage and mass loss. According to the forms of radiation damage, methods have been proposed to reduce or even avoid the damage, such as using smaller condenser apertures, increasing accelerating voltage, and carbon coating the surface on both sides. This work will help understand the data collected from TEM observation of nanocement, and provide useful suggestions for performing future
in-situ TEM studies of the hydration reaction of nanocement particles.

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References


