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Study of the in-situ growth of carbon nanofibers on cement clinker

Xiaoyin Cao, Xiaodong Li, Suhua Ma and Xiaodong Shen

Abstract

Because fibres are difficult to disperse evenly in cement-based materials, we attempted to grow carbon nanofibers (CNFs) in situ on Portland cement clinker particles using chemical vapor deposition (CVD). The results show that the phase compositions and alite polymorph didn’t change for the Portland cement clinker treated at 600 °C in the atmosphere of blended gas containing argon (Ar), hydrogen (H₂) and acetylene (C₂H₂). The CNFs was successfully grown in situ on the Portland cement clinker due to the reaction of C₂H₂ in the presence of H₂. The diameter and length of the CNFs were 20–30 nm and 0.6–0.9 μm respectively. C₃S is the main component of cement clinker. The hydration of C₃S plays a crucial role in the performance of cementitious composites. The hydration of C₃S was significantly delayed and reduced due to the incorporation of CNFs.

1. Introduction

Cement-based materials are believed to be one of the most important materials in the field of construction due to their relative low price and satisfactory workability. However, cement-based materials are also quasi-brittle and usually have low tensile and flexural strengths. These materials have interior and surface defects, making it easy to crack and fracture under extreme conditions.

With the rapid development of nanotechnology, the properties of cement-based materials were improved. Carbon nanotubes (CNTs) and CNFs have been utilized in cement-based materials [1–4]. Camacho et al [5] found that CNTs increased the bending and compressive strength of mortar and also improved the resistance of hardened cement pastes to carbonization and chloride attack. Lee et al [6] obtained a composite materials made of cement and multi-walled carbon nanotubes by mix-grinding carbon nanotubes and cement powder in a planetary ball mill. Makar et al [7] distributed single-walled carbon nanotubes (SWCNTs) on the surface of ordinary Portland cement (OPC) particles and investigated the hydrated OPC/SWCNT composites at a water to cement ratio of 0.5. The obtained results indicated that the SWCNTs accelerated C₃S hydration and also altered the morphology of the hydration products. The SWCNTs were observed to pull out of the composite in the fibre form after hydration of 24 h, which explained the enhanced performance of the composite. Li et al [8] studied the damping properties of CNT-incorporated cement-based materials. The experimental results showed that the flexural strength index of the CNT/cement composites was higher than that of pure cement slurry, and the incorporated CNTs increased the vibration-reduction capacity of the cement slurry. However, due to their ultrafine size, Van der Waals forces among the various carbon nanomaterials make it tend to agglomerate. The chemical structure of the carbon is hydrophobic, so it does not interact with the cement powder [9]. Therefore, it is difficult to uniformly disperse carbon nanomaterials in cement matrices. It was reported that by using CVD method, graphene has been successfully synthesized on glass substrates, improving the performance of the resulting inorganic materials [10–13]. And carbon nanomaterials have also been grown on cement substrates [14–17]. Methane(CH₄) and C₂H₂ can be used as the carbon source to synthesize carbon nanomaterials via CVD [18, 19]. Graphene can be synthesized on SiO₂ by ambient CVD, and the resulting graphene films have been used in dye-sensitized solar cells [20]. The direct growth of graphene improved electrical and thermal conductivity and surface hydrophobicity of glass [10, 12].
In this research, it was attempted to make CNFs grow \textit{in situ} on cement clinker particles by using atmospheric pressure CVD, improving the properties of the cement clinker. X-ray fluorescence spectrometry (XRF) and x-ray diffraction (XRD) were used to measure the chemical compositions and phase structure. Raman spectroscopy, thermo-gravimetric analysis (TG) were used to evaluate the quality of the carbon nanomaterials, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Fourier transform infrared spectroscopy (FT-IR) were used to characterize CNFs. Isothermal calorimeter was used to determine the heat evolution.

2. Experimental section

2.1. Raw materials
The Portland cement clinker used in the experiments was supplied by Wuxi Nanjing Cement Co., Ltd (China). The chemical composition of the clinker was determined by XRF, and the result is listed in table 1. The untreated Portland cement clinker is denoted as C0. Ar, H2 and C2H2 were provided by Nanjing Shangyuan Co.

2.2. Sample preparation
To study the \textit{in situ} growth of the CNFs in the cement clinker, the CVD method was used in this work. During this process, C2H2 and Ar were chosen as the carbon source and carrier gas, respectively. The treatment experiments were conducted in a quartz tube furnace (Lindberg/Blue M, HTF55322C, Asheville, NC, USA). The detailed procedure is as followed: (1) The Portland cement clinker was weighed in a quartz crucible and placed in the tube furnace with a vacuum; (2) The Portland cement clinker was heated up to 600 °C under an Ar atmosphere; (3) At 600 °C, C2H2 and H2 were inlet into the tube furnace and kept for 1 h; (4) After that, the C2H2 was immediately switched off, and H2 was switched off at 200 °C. Two flow regimes were adopted, the flow unit is Standard Cubic Centimeters per Minute (sccm): C1: 20 sccm of C2H2 + 50 sccm of H2; C2: 50 sccm of C2H2 + 20 sccm of H2. Ar was inlet with a flow rate of 50 sccm. The illustration for the treatment of the Portland cement clinker is shown in figure 1.

2.3. Methods
Oxide contents of clinker were obtained by XRF (ADVANT’XP, American Thermoelectric Group Switzerland ARL) with GN rhodium target, ultra-tip, ultra-thin window (75 μm), end-window x-ray tube, solid-state 3.6 KW high-power generator.

The XRD patterns were obtained by using a Rigaku SmartLab 3000 A diffractometer with a 600 W Cu Kα radiation source ($\lambda = 0.154$ nm with scan speed = 5° min$^{-1}$; voltage 40 kV, current 15 A, data were collected from 10° to 70°).

SEM (JSM-6510 scanning electron microscope with tungsten filament and an accelerating voltage of 15 kV) was used to observe the morphology of the samples. The samples were coated with gold for 160 s prior to SEM examination.

TEM (TF20, JEOL 2100F transmission electron microscope (USA) with accelerating voltage of 200 kV) was used to characterize the microscopic appearance and length of carbon materials.

The quality of the carbon materials was tested by Raman spectroscopy (LabRam HR Evolution; LabRam ARAMIS, wavelength 514 nm and data collection from 300 to 3000 cm$^{-1}$).

| Chemical Oxide (%) | C0   | C1   | C2   |
|-------------------|------|------|------|
| CaO               | 66.70| 61.30| 51.78|
| SiO2              | 21.05| 18.19| 14.58|
| Al2O3             | 5.48 | 4.85 | 3.88 |
| Fe2O3             | 3.45 | 3.70 | 3.43 |
| MgO               | 1.16 | 0.81 | 0.63 |
| K2O               | 0.48 | 0.59 | 0.62 |
| TiO2              | 0.31 | 0.27 | 0.24 |
| Na2O              | 0.28 | 0.22 | 0.18 |
| SO3               | 0.37 | 0.32 | 0.35 |
| P2O5              | 0.21 | 0.14 | 0.12 |
| MnO2              | 0.062| 0.060| 0.059|
| LOI               | —    | 6.95 | 24.2 |
FT-IR spectra were recorded from 4000 to 400 cm⁻¹ using a Nicolet-IS5 spectrometer via the KBr-disk technique.

A simultaneous TG/DSC thermal analyser (TGA/DSC1/1600LF) was used to measure weight loss, and samples were heated from 40 to 1000 °C with a uniform heating rate of 10 °C min⁻¹ under air atmosphere.

In order to investigate the effect of in situ growth of CNFs on hydration, the 5% gypsum (Wuxi Nanjing Cement Co., Ltd.) were added into Portland cement clinker with and without treatment, respectively. An 8-channel isothermal calorimeter operating at 20 °C (TAM Air; Thermometric AB, Sweden) was used to determine the heat evolution of samples. The water to cement ratio of 0.5 was determined. The specimens were mixed with deionized water by using a mixing machine for 2 min. Approximately 4 g of paste were weighted in a sealed glass ampule, then transferred into the isothermal calorimeter as soon as possible and measured over a period of 3 days. The mechanical properties are characterized by compressive strength and flexural strength.

3. Results and discussion

3.1. Effect of treatment on phase assemblages of Portland cement clinker

The chemical compositions of samples without and with treatment are given in Table 1. There is no mass loss for the Portland cement clinker before treatment. After treatment, there is 6.95% and 24.2% mass loss for samples. It indicates that some new components were incorporated into the Portland cement clinker. And these new components are apt to volatilize if the samples are heated.

As shown in Figure 2, the surfaces of Portland cement clinker are covered with new components after the treatment. It seems that the new components are more for sample C2 (Figure 2(d)), compared to sample C1 (Figure 2(c)). However, the new components were not observed in XRD patterns (Figure 3). The assemblages in treated samples are the same to those in the Portland cement clinker, including C3S, C2S, C3A and C4AF. This result indicates that the new components are amorphous or poor crystallinity.

3.2. Effect of treatment on alite polymorphs of Portland cement clinker

C3S is the main mineral phase of Portland cement clinker. In order to observe the changes in the structure of C3S, the crystal form of C3S is analyzed by XRD. The characteristic peaks of C3S are given in Figure 4. Generally two intervals of 32°–33° (Figure 4(a)) and 51°–52° (Figure 4(b)) are used to determine the crystal form of C3S [21]. There are also other sections where the crystal form of C3S can be judged. The two peaks at 24.5°–26.5° correspond to polymorph M1, while the other polymorphs just have one peak. An obvious peak at approximately 28° corresponds to polymorph M3 [22]. In this experiment, peaks at 32°–33° and 51°–52° (in Figure 4) are similar to the mixed crystal structure of M1 and M3 reported in the literature [21, 23]. There is only one peak at 24.5°–26.5° (Figure 4(c)), and no obvious peaks around 28° (Figure 4(d)). Therefore, the polymorph of C3S is a mixture of M1 and M3 for the Portland cement clinker. In addition, the peaks shown in the range of 55.5°–57.5° (Figure 4(e)) are consistent with those of the mixture of M1 and M3 [24]. Furthermore, the patterns of the three samples are similar, indicating that the treatment does not have a substantial effect on the polymorphs of the C3S. At the same time, the intensity of the peaks changed slightly for C1 and C2, compared to the Portland cement clinker without treatment. That is due to the samples of C1 and C2 contain amorphous components.
3.3. **In situ growth of carbon fibres in the Portland cement clinker**

It is known from table 1 and figure 2 that new substances are generated. In order to further understand what new substances are, FT-IR tests were performed. Three main peaks are present for treated samples and four peaks for untreated sample in the FT-IR spectra shown in figure 5. The peak at 3437 cm$^{-1}$ is attributed to the stretching vibration of O–H bonds in the absorbed water. The peak at 925 cm$^{-1}$ corresponds to the stretching vibration of the Si–O bond, while the peak at 523 cm$^{-1}$ is the bending vibration of the Si–O group [25]. The peak (for blank spectrum) at 3645 cm$^{-1}$ is ascribed to Ca(OH)$_2$ because of the hydration of Portland cement clinker in the air [26]. The peak is not present in the other two spectra because the simples were treated at 600 °C for 1 h [27]. No new bonds were found in samples C1 and C2. The intensities of peaks at 925 cm$^{-1}$ and 523 cm$^{-1}$ decreases due to the incorporation of new components.

In order to identify the new components incorporated into the Portland cement clinker, the Raman spectra are given in figure 6. Two peaks were observed in the Raman spectra of samples C1 and C2. The D band (at approximately 1300 cm$^{-1}$) is attributed to the defects in the graphite, and the G band (at approximately 1580 cm$^{-1}$) is attributed to the normal graphite [28]. These results demonstrate that graphite grows *in situ* on the
Portland cement clinker, which is accordant with these reports [29, 30]. In this process of treatment, C$_2$H$_2$ is decomposed to produce precursors [30], which then grow into carbon materials as shown in the equation (1) [15, 30–32]. Not all of carbon particles can form normal graphite, which is depends on the experimental gas and the catalyst [30]. The relative intensities of both the D and G peaks reflected the defect degree of carbon material [33]. The ratio of $I_D/I_G$ by calculating the area of the two peaks. The value of $I_D/I_G$ in C1 is 2.64 and the ratio in C2 is 5.16. The higher ratio of H$_2$/C$_2$H$_2$ is the fewer defects are. According to previous research, H$_2$ can effectively control the shape and dimensions of the carbon species because it acts as cocatalyst [34].

\[ C_nH_m \rightarrow C + H_2 \]  

The kinds of carbon material are various, such as CNFs, CNTs, and graphene. So as to identify carbon material, a TEM analysis was used. TEM pictures show that the carbon materials are CNFs and some carbon particles in figure 7. The diameter of the CNFs is nearly 20 nm for sample C1, while the diameter is 30 nm for...
The lengths are 0.6 to 0.9 μm, respectively. Hence, the increased flow rate of C₂H₂ and H₂ also contributes to the size of the CNFs. In addition, the contents of CNFs in the sample C₂ are more than those in C₁. It can be explained that acetylene as the carbon source directly affects the amount of carbon deposited. This result was verified further by TG analysis (figure 8). The major weight loss between approximately 400 °C and 550 °C are attributed to the oxidation reaction of amorphous carbon and CNFs [29, 35]. In all the investigated samples, sample C₂ has the highest weight loss.

### 3.4. Hydration kinetics of samples

Figure 9 presents the heat flow and cumulative heat curves of different samples. Two peaks were observed in heat flow curves of the samples (figure 9(a)). The first peak occurred in 30 min is attributed to a combination of exothermic wetting and the formation of trisulfide hydrated calcium sulfoaluminate (AFt) phase. The second peak is mainly associated with the hydration of C₃S [36]. C₃S is the main component of Portland cement clinker, usually accounting for 50%–70% of Portland cement clinker by weight. One of its main hydration products, calcium silicate hydrate(C–S–H), is the bonding part in the cement-based materials, which is responsible for the

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**Figure 5.** FT-IR spectra of the samples.

**Figure 6.** Raman spectra of samples.
Figure 7. TEM images of (a) C1 and (b) C2 and distribution of carbon in samples (c) C1 and (d) C2.

Figure 8. TGA curves of the samples.

Figure 9. Heat release of cement pastes.
strength and durability development of the cement-based materials. Hence, the hydration of C₃S plays a crucial role in the performance of cementitious composites. Compared with the blank sample, the heat flows of C₃Si in sample C₁ and simple C₂ were significantly delayed and suppressed. Exothermic hydration increases with the content of carbon fiber [37, 38]. So the delayed and reduced hydration of C₃S might be caused by carbon particles. In addition, the cumulative heat releases of C₁ and C₂ at 72 h are 591.58 J g⁻¹ and 626.88 J g⁻¹, respectively, which are 31.57% and 27.49% lower than the blank sample (figure 9(b)). In the first 35 h, the heat release of C₂ is lower than that of C₁, because the carbon particles in the early stage inhibit the hydration. CNFs play a major role after 35 h. Therefore, the treatment conditions should be regulated further to promote the growth of CNFs.

3.5. Mechanical properties of samples
According to the hydration exothermic curves, the sample C₂ and the blank sample were selected to mix with 5% gypsum respectively to make cements. Their compressive and flexural strength are given in figure 10. Either compressive strength or flexural strength is higher for the cement made of sample C₂ than that of the cement made of blank simple at 3 days. However, the strength of the cement made of sample C₂ are less at other curing ages.

4. Conclusion
The growth of CNFs on the cement clinker was investigated. It was found that CNFs can be successfully synthesized on the surface of cement clinker by CVD. And this process did not affect the chemical composition and crystal form of Portland cement clinker. The amount of C₂H₂ and H₂ play a crucial role in the quality of the synthesized CNFs. The content and morphology of CNFs can be controlled by adjusting the flow rate of the two. The amount of deposited carbon increases as the carbon source increases. Increasing the proportion of H₂ is useful for the treatment of normal graphite. The presence of carbon particles delayed and suppressed the hydration of C₃S. Increasing the content of CNFs is expected to improve hydration exotherm. C₂ has an improvement effect on the strength at the curing age of 3 days. However, there are many aspects need to be explored in the future, such as the mechanism of CNFs in cement hydration and functional application of cement CNFs-grown clinker.

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ORCID iDs

Xiaoyin Cao https://orcid.org/0000-0001-6283-077X

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