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Review

In situ growth of carbon nanotubes/carbon nanofibers on cement/mineral admixture particles: A review

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HIGHLIGHTS

- We review research progress of the in situ growth of carbon nanotubes (CNTs)/nanofibers (CNFs) on cement/mineral admixture.
- The methods and theories of in situ growth of CNTs/CNFs on cement/mineral admixtures are systematically presented.
- The properties of the cement-based composites fabricated with the CNTs/CNFs-grown cement/mineral admixture are summarized.
- The issues about the in situ growth of CNTs/CNFs on cement/mineral admixture needed to be further studied are discussed.

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ABSTRACT

Carbon nanotubes (CNTs) and carbon nanofibers (CNFs) are beneficial reinforcement materials for high-performance and multifunctional cement-based composites. However, it is difficult to uniformly disperse CNTs/CNFs in cement-based composite during the composite fabrication process due to CNTs/CNFs aggregation. The in situ growth of CNTs/CNFs on cement/mineral admixture provides a new method to solve this issue. This article summarizes the methods and theories of in situ growth of CNTs/CNFs on cement/mineral admixture, including chemical vapor deposition method and microwave irradiating conductive polymers method. Properties of the cement-based composites made from the CNTs/CNFs-grown cement/mineral admixture are presented. The issues about the in situ growth of CNTs/CNFs on cement/mineral admixture that needed to be further studied are discussed.

Contents

1. Introduction

Cement-based material is a quasi-brittle material according to the macroscopic mechanical behavior. There exist many defects interiorly and on its surface. Its tensile, shear and impact resistance are weak. Under the effect of the load, temperature, humidity and

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other factors, the cement-based material is easy to crack and fracture. The traditional solution is mainly to use steel or millimeter/micron fiber (such as steel fiber, carbon fiber, and polyvinyl alcohol fiber) to reinforce the cement-based materials. However, researchers recognized that micro-sized reinforced materials can only limit the expansion of internal microcracks of cement-based materials instead of preventing the microcracks from engendering. The addition of carbon nanotubes (CNTs) and carbon nanofibers (CNFs) can address the problems mentioned above. CNTs/CNFs can transfer the reinforcement and modification behavior on the cement-based materials from microscale to nanoscale. CNTs/CNFs possess better mechanical property, whose elastic modulus, tensile strength and ultimate deformation are respectively 10, 20 and 18 times that of microscale carbon fiber. The inter-laminar shear strength of the CNTs/CNFs and the epoxy resin layer is an order of magnitude higher than that of micro carbon fiber and the epoxy resin layer [1–3]. Li et al. firstly observed that the addition of 0.5 wt.% CNTs can respectively improve the flexural, compressive strength and the failure strain by 25%, 19% and 27%. Raki et al. reported that CNTs can improve the Vivtorinox hardness of the early hydration of cement-based material by 600%, the Young modulus by 227% and the flexural strength by 40% [2]. Veedu incorporated 0.02 wt.% CNTs into the cement-based materials to make its flexural and compressive strength increase by 30% and 100% [3]. Chaipanich et al. firstly used CNTs of 0.5% and 1% by weight in a fly ash cement system to produce carbon nanotubes-fly ash composites in the form of pastes and mortars and found that the use of carbon nanotubes results in higher strength of fly ash mortars [4]. Shah et al. only added 0.048–0.08 wt.% CNTs into cement-based materials to increase its flexural strength and elastic modulus by 8–40% and 15–55% [5,6]. Gay and Sanchez founded that the split tensile strength of the cement-based materials with the addition of 0.2 wt.% CNFs is 26% higher than that of the cement-based materials with fly ash [7]. Kumar et al. discussed the effect of multiwalled CNTs on strength characteristics of the hydrated Portland cement paste [8]. Gao et al. founded that the compressive strength of the CNFs reinforced concrete with the addition of 0.16 wt.% CNFs was 42.7% higher than that of ordinary concrete. Researches pointed out that CNTs/CNFs achieves enhancement effect by nucleation, increasing the amount of C–S–H gel of high hardness, improving pore structures, controlling nanoscale cracks, improving the early strain capacity and reducing autogenous shrinkage, etc. [1–3]. These mechanisms also would improve the durability of the cement-based materials. Han et al. have founded that the addition of CNTs could improve the transport properties of the cement mortar. In addition, due to the excellent electrical, thermal, electromagnetic properties of the CNTs/CNFs, it could make the cement-based materials possess electrical, thermal, electromagnetic and sensing properties, and then make the cement-based materials possess multi-functional properties [1,3].

However, CNTs/CNFs are easy to agglomerate due to its high specific surface energy. Therefore, effective dispersion methods are needed to disperse CNTs/CNFs into the cement-based materials in order to fully implement enhancement effect of CNTs/CNFs. To solve the problem, researchers carried on a lot of studies and obtained some effective methods, such as physical dispersion methods (including high-speed shear and ultrasonic dispersion), chemical dispersion methods (surface covalent bond modification with strong acid treatment or non-covalent bond modification with surfactants, etc.), and the combination of physical and chemical methods [1–3]. However, the above methods only can improve the dispersion effect to some extent. In addition, there exist some other disadvantages such as high energy consumption, decreasing aspect ratio, etc. [9–11]. Recently researchers put forward a new method to solve the dispersion problem of CNTs/CNFs, which is to make CNTs/CNFs and cement/mineral admixture a whole by in situ growing CNTs/CNFs on the cement/mineral admixture particles.

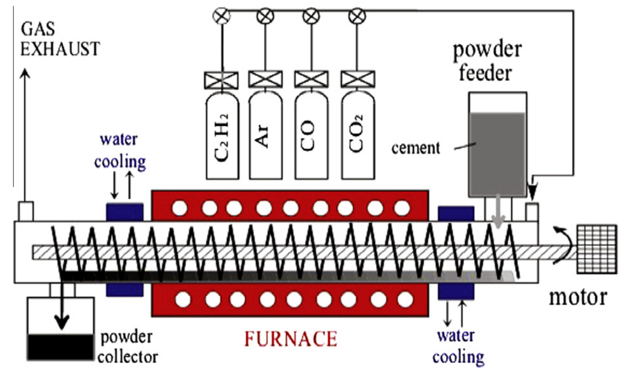

Fig. 1. Schematic representation of experimental setup with continuous feeding of cement particles using a screw feeder for the CVD in situ CNTs/CNFs growth [14].

This article summarizes the studies of in situ growth of CNTs/CNFs on cement/mineral admixtures, including the methods and theories of in situ growth of CNTs/CNFs, and the properties of the cement-based materials prepared with the addition of the CNTs/CNFs-grown cement/mineral admixture.

2. Methods of in situ growth of CNTs/CNFs on cement/mineral admixture

The research on the in situ growth of CNTs/CNFs on the cement/mineral admixture mainly contains the in situ growth of CNTs/CNFs on cement, silica fume, clinker, fly ash, etc. The methods of in situ growth of CNTs/CNFs include chemical vapor deposition method and microwave irradiating conductive polymers method.

2.1. Chemical vapor deposition method

Chemical vapor deposition (CVD) method, also called hydrocarbon gas pyrolysis method, is making gaseous hydrocarbon passing through the template attached with the catalyst particles under the condition of high temperature, where the gaseous hydrocarbon decomposed to produce CNTs/CNFs.

Nasibulin et al. firstly employed CVD method to grow CNTs/CNFs on the surface of cement, in which cement with catalyst is heated to grow CNTs/CNFs in the carbon source gas environment. Because cement contains Fe_2O_3, SiO_2, MgO and Al_2O_3 etc. catalytically materials for the growth of CNTs/CNFs, no external catalyst is needed for the in situ growth of CNTs/CNFs. They proposed a set of reactor system (as shown in Fig. 1) which is able to continuously feed the matrix material. The detailed process is as following: (1) acetylene was used as the carbon source gas passing through the reactor; (2) Sulphate-resistant cement with 4% Fe_2O_3 was introduced into the quartz tube reactor with a powder feeder; (3) The temperature of the resistively heated furnace was kept in the range of 400–700 °C; (4) At the end of the reactor system a powder collector was used to collect products. The experimental results indicated that no carbon precipitated on particles below 450 °C;

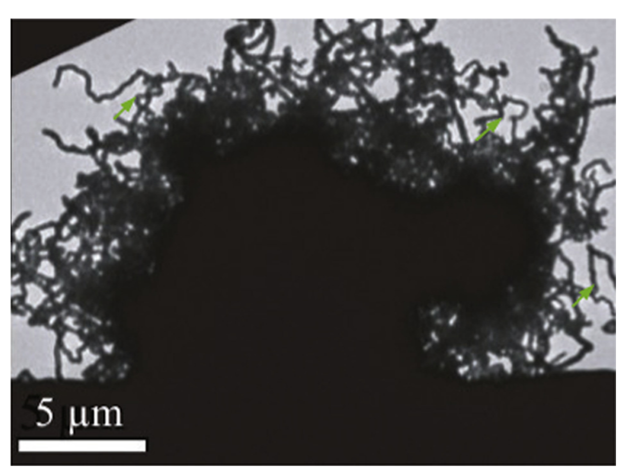

Fig. 2. TEM image of complete coverage of the cement particles by CNTs/CNFs [14].